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ELEMENTARY QUALITATIVE ANALYSIS

for

COLLEGE STUDENTS

BY

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PREFACE

This book is an attempt to put in printed form the system of laboratory and quiz room instruction that has been developed during recent years in the elementary courses in Qualitative Analysis at the University of Illinois. It presumes that the student has had the equivalent of not less than five semester hours of college chemistry, and that he is able to follow laboratory directions with a reduced amount of oversight on the part of the instructor.

The fundamental purpose in the compilation of this manual has been to enable the student to know at all times exactly what he is doing. The notion, occasionally heard, that the function of a course in qualitative analysis is to "teach a student to follow directions" is rejected, not only because it is a purely mechanical approach to the subject, but also because it is perversive of the best development of the student. There is too great a tendency, even in the best of our teaching, for the student gradually to accept the attitude that analytical procedures are more or less unintelligible processes, which, if carefully followed, will in the end tell what the ingredients of a substance are. In order to anticipate and, as far as possible, prevent such an attitude, the preliminary experiments have been designed to set forth in simple, independent tests the fundamental reactions involved in analytical work; and lists of simple exercises have been included to direct attention to these reactions. Theoretical discussions to explain results are given as notes, placed as close to the experimental directions as possible.

The endeavor has been made to put nothing in this book that the elementary student might not be expected to understand. The notes and general discussions have been prepared with great care, and the writer feels that the instructor should not allow the students to slight this very important part of the work. Students should be given to understand at the beginning that they will be held accountable for the notes on all the procedures

assigned by the instructor, and the latter should not fail in his part to quiz them constantly on these discussions.

A number of paragraphs have been included that may be omitted at the discretion of the instructor, without in any way involving the continuity of the analytical procedure. Most of these have to do with the detection of the less common ions, and a few of them require more or less dangerous reagents. Such paragraphs have been marked with asterisks.

The procedures in this manual have been chosen with a view to their reliability in the hands of elementary students. For the most part, they are methods found in other manuals, but reproduced here with many modifications or adaptations in favor of the beginning student. Some of the procedures are new to elementary manuals. Method A for the Tin Subgroup has been adapted from the very satisfactory quantitative procedure of Clarke for separating tin from arsenic and antimony, and has been found at the University of Illinois to give better results than other procedures. A new procedure for the analysis of the Iron Subgroup in the presence of phosphates and oxalates is also included. The general scheme for the detection of the anions is, with certain changes, the one worked out by this writer and published in the seventh edition of W. A. Noyes' "Qualitative Analysis" (Henry Holt and Company). In two cases it has been felt worth while to give alternative methods. The method of A. A. Noyes has been included as an alternate procedure in the Tin Subgroup, and the Gooch-Browning method for the separation of Ca^{++} from Sr^{++} by means of potassium ferrocyanide as an alternate procedure in Cation Group IV.

The writer is glad to acknowledge his debt to the large group of instructors and assistants at the University of Illinois who have collaborated so enthusiastically in trying out the new procedures; to Dr R. W. Hufferd of DePauw University for suggesting the use of the Vogel test for Co^{++}; and particularly to Drs. T. E. Phipps and L. F. Yntema of the University of Illinois for criticism of the manuscript and for many suggestions that have been incorporated in these pages.

J. H. Reedy

Urbana, Illinois,
August, 1924.

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INTRODUCTION

The purpose of **Qualitative Analysis** is to ascertain the elements or groups (*i.e.*, radicals) which are present in a given substance. The examination should be quantitative to the extent that the student should distinguish between the main components of the material, which are present in relatively large amounts, and those constituents which are present in small quantity, perhaps only as traces.

Since most of the processes involved in ordinary qualitative procedure are reactions between solutions, the actual tests as usually carried out are tests for the ions and not for the elements themselves. Metals are usually present in a solution as cations, bearing charges of positive electricity; *e.g.*, sodium as Na^+, or iron as Fe^{+++}. Occasionally, however, metals appear in complex anions, as iron in ferrocyanides, in which the metal occurs in the complex anion, $Fe(CN)_6^{----}$. The non-metals, with the exception of hydrogen in acids and nitrogen in the ammonium group, are uniformly present in anion groups.

In general, a metallic ion must be separated from other metallic ions before a conclusive test may be made for its presence. This separation is carried out in a systematic way, first by precipitating the cations in groups, and later by separating the groups into their component ions. After a solution containing the ion in question, free from all interfering ions, has been obtained, the *specific test* for the ion is made. If this test is not sufficiently sensitive, or if it is obscured by failure to have the solution free from interfering substances, a *confirmatory test* is made. It follows from this that a confirmatory test should be either more delicate than the first test, or else be free from interferences by the other substances present in the solution. Later in the course it will be pointed out how, when a test appears weak and indecisive, it may be accurately interpreted by comparison with a *blank test* and a *control test*. In the former the test reagent is applied to a liquid (usually water) free from the

ion in question; in the second, the test is made on a very dilute solution containing the ion. By comparing the actual test with the blank and control tests, the presence of the ion which is being tested for may be decided with certainty.

For the most part, the separations in analytical chemistry are made by converting the ions of the solution into compounds which have wide differences in solubility. For example, Ba^{++} may be separated from Cu^{++} by adding a solution containing the SO_4^{--} anion. It may be assumed that there is a tendency for both $BaSO_4$ and $CuSO_4$ molecules to form in the solution; but since the former is insoluble in water, while the latter is soluble, only the Ba^{++} is precipitated. It follows, then, that analytical procedures are based, largely if not wholly, on differences in solubility, and the student should learn to interpret these procedures in the light of solubility relationships. Frequent reference will be made to the Solubility Table on page 122.

Solubility is of two kinds: physical and chemical. In physical solution, no chemical change is involved, and the original substance may be regained by simply evaporating or otherwise removing the solvent. Examples are easy to enumerate: salt in water, sulfur in carbon disulfide, bromine in ether. In chemical solution, on the other hand, the substance is converted into a new compound by a reaction which may be expressed by a chemical equation, and, in most cases, the original cannot be restored by evaporation or any other purely physical process. For example: In the solution of limestone by hydrochloric acid, the reaction proceeds according to the equation: $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$ (gas). Upon evaporation, the residue is not the original $CaCO_3$, but a new substance possessing properties quite different from the first.

TERMS USED IN CHEMICAL ANALYSIS

Reagent.—A substance used to produce a definite change in the material under consideration. The change is the *reaction.* An example is: HCl is the reagent for the ions of Cation Group I. The formation of the precipitate containing these ions is the reaction.

Precipitation.—The formation of a solid by the action of a reagent on a solution. Slight precipitates may appear as a tur-

bidity. Sometimes a precipitate is so finely divided that it may clog up the pores of a filter paper, or even pass through them. Graham called such a precipitate "colloidal," because of its gluey or gummy consistency.

Filtration.—The separation of a precipitate and a liquid by allowing the latter to pass through a medium that will retain the former. The commonest medium for this purpose is "filter paper"—paper from which all mineral matter has been removed by washing with acids. Asbestos, glass wool, and other materials are used for solutions which would attack paper. The liquid which runs through the paper is called the *filtrate*, and the solid remaining on the filter the *precipitate* or *residue*.

Decantation.—The pouring off of the "supernatant" liquid from a precipitate. This is a rapid means of separation in cases where the precipitate settles well. As rule, the liquid is poured through a filter so as to prevent the loss of any loose particles.

Washing.—The pouring of water or other liquid over a precipitate to wash out soluble materials. The liquid should be used in small portions, and the solid allowed to drain well before repeating the extraction.

Digestion.—Allowing a solid to remain for some time in a solution, either with or without heating, so that a slow reaction may have time to complete itself.

Ignition.—The strong heating of solids. The chemical use of this term is quite different from the ordinary one, which means "setting fire to." Ignition in chemical procedures is, therefore, carried out by applying heat beneath the vessel containing the substance to be ignited, and *not within it.*

LABORATORY DIRECTIONS

The Laboratory Outfit.—After a desk has been assigned, obtain the key from the storeroom. Check the apparatus in the desk against the list furnished you. In case any articles are broken or missing, report the fact to the laboratory instructor, who will issue an order to the storekeeper to furnish them. Then sign the apparatus list and turn it in at the storeroom.

Keep the outfit in the desk in as orderly condition as possible.

Wash all glassware as it is returned to the cupboard, so that it will be ready for instant use when needed.

Replace any broken apparatus at once by purchases from the storeroom, thereby keeping a complete outfit in the desk.

Wash Bottle.—Prepare a wash bottle according to the following directions: Fit a 500-cc. flat-bottomed Florence flask with a two-holed rubber stopper. Bend[1] a piece of glass tubing 15 cm. long in the middle to an angle of about 120 deg. to make the mouthpiece *A* (see Fig. 1). For the delivery tube *B*, take another piece, about 25 or 30 cm. long, and bend it near

Fig. 1.—Wash bottle.

Fig. 2.—Bending glass tubing.

one end to an angle of about 60 deg. About 15 cm. below this bend make a slight bend, so that the tube, after the extra length has been cut off, will extend just to the bottom of the flask as shown in the figure. Cut the nozzle end of the tube off rather short—about 3 cm. from the bend. Take a piece of glass tubing 15 or 20 cm. long, and heat it near its middle in the colorless Bunsen flame, rotating it constantly, until it softens. Remove from the flame and pull the ends apart very slowly, so as to reduce the size of the heated portion, as shown in Fig. 3. After the tube has cooled, make a scratch with a file (be careful not to crush the tube) at the narrowest part and break. Cut off the rest of the tube so that the nozzle will be about 5 cm. long. Fire-polish the ends of all these pieces by heating them in the flame until the glass just begins to soften, being careful not to close the jet of the nozzle by melting together the thin wall of glass. Connect the nozzle with the delivery tube by a piece of rubber tubing 3 or 4 cm. long. This should bring the nozzle close

Fig. 3.—Making the nozzle.

[1] All bends should be made with the flat, luminous flame, formed by using the wing top and closing the air holes at the base of the burner. *A* and *B* (Fig. 2) show the results of the wrong and the right methods of bending glass tubing.

enough to the neck of the flask for it to be manipulated by the first and second fingers of the hand holding the flask.

Rinse the bottle once, and then fill with distilled water. *Use distilled water sparingly.* The following are the more important procedures in which distilled water is used:

1. Rinsing apparatus (after washing with tap water).
2. Washing precipitates.
3. Diluting solutions.

ELEMENTARY QUALITATIVE ANALYSIS

PART I

DETECTION OF THE IONS OF THE METALS

GROUPS OF THE METALLIC IONS (CATIONS)

Systematic analysis of a solution for metallic ions consists, as a first step, in adding to the solution certain reagents, called "group reagents," which precipitate these ions in groups. These groups are as follows:

Group I.—Cations which form chlorides insoluble in water and in dilute acids: *lead*, *silver*, and *mercurous mercury*. The group reagent is dilute hydrochloric acid. The group is called "The Hydrochloric Acid Group."

Group II.—Cations which form soluble chlorides, but whose sulfides are precipitated from dilute acid solution by hydrogen sulfide: *mercuric mercury*, *lead*, *bismuth*, *cupric copper*, *cadmium*, *tin*, *arsenic*, and *antimony*. The group reagent is hydrogen sulfide (in the presence of dilute hydrochloric acid). The group is called "The Hydrogen Sulfide Group."

Group III.—Cations whose sulfides are not precipitated from dilute acid solutions by hydrogen sulfide, but whose sulfides or hydroxides are precipitated from solutions containing ammonium salts by ammonium hydroxide and hydrogen sulfide (*i.e.*, ammonium sulfide): *aluminium*, *chromium*, *zinc*, *manganese*, *iron*, *nickel*, and *cobalt*. The group is called "The Ammonium Sulfide Group."

Group IV.—Cations whose sulfides and hydroxides are soluble, but whose carbonates are insoluble in solutions containing

ammonium salts: *barium*, *strontium*, and *calcium*. The group reagent is ammonium carbonate (in the presence of ammonium salts). The group is called "The Alkaline Earth Group;" also "The Ammonium Carbonate Group."

Group V.—Cations whose chlorides, sulfides, hydroxides, and carbonates are soluble, either in water or in solutions containing ammonium salts, and therefore are not precipitated by any of the foregoing group reagents: *magnesium*, *potassium*, *sodium*, and *ammonium*. It should be noted that this group has no group reagent. It is called "The Soluble Group."

Note.—Lead occurs in both Group I and Group II. Its presence in the latter group is due to a slight solubility of its chloride in water, with the result that its precipitation in Group I is not complete. Mercury also occurs in Groups I and II, but for a different reason, *viz.*: Mercury forms two cations, Mercurous, Hg_2^{++}, and Mercuric, Hg^{++}; the chloride of the first is insoluble in water, while the chloride of the second is soluble. Consequently, they fall into different groups.

DETERMINATION OF THE CATION GROUPS IN A SOLUTION
PRELIMINARY EXPERIMENTS

Note.—In performing the experiments in this course, the student should keep a concise and intelligible record of the results of each experiment. For his guidance, questions to be answered are indicated by (?), equations to be written by (E), references to be consulted by (R), and special instructions in technique by (Instructions). These notes should be made as the experiment progresses, and not at the end of the hour, or outside of the laboratory. The student should be encouraged to bring his textbook to the laboratory for use as reference. See Appendix (pages 117, 118) for suggested forms of records.

(1) **Group I.**—Use $AgNO_3$ solution as representative of this group. Place 2 cc. of this solution in a test tube, dilute with about 10 cc. of water, and slowly add dilute HCl, with shaking, as long as the precipitate seems to increase in amount. Filter,[1]

[1] In order to obtain satisfactory results in filtering, the student must be particular about his technique. Most funnels have an angle of 60 deg. at their apex, so that by folding the paper twice (see Fig. 4), the paper should fit the funnel exactly. In case the funnel is not exactly 60 deg., a little practice will show how to fold a paper so as to make a perfect fit. The dry paper should be placed in the funnel and moistened with distilled water, and the folds of the paper carefully pressed with the fingers so as to make the

and test for the completeness of the reaction by adding a few drops of dilute HCl to the filtrate. If more AgCl forms, filter again. Place the filtrate in a 250-cc. Erlenmeyer flask and saturate with H_2S.[1] From the result infer whether AgCl is soluble in water or not (?).

---

paper exactly conform to the walls of the funnel. This technique will not only insure better but usually faster filtration.

Another very important point in the technique of filtering is the prevention of spattering. The liquid to be filtered should not be poured directly into the funnel, but down a stirring rod held against the lip of the vessel. Further, the stem of the funnel should touch the side of the beaker receiving the filtrate, so that the liquid will run down the side of the beaker and not fall freely. Both of these points are shown in Fig. 5.

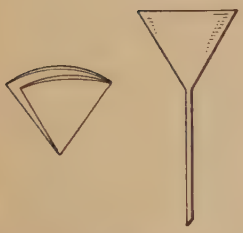

FIG. 4.—Fitting a paper in a funnel.

FIG. 5.—Preventing spattering.

FIG. 6.—H_2S precipitation flask.

[1] Precipitation with H_2S is carried out in the apparatus shown in Fig. 6. The outfit consists of a 250- or 300-cc. Erlenmeyer flask fitted with a one-holed rubber stopper carrying a glass tube which extends just through the stopper. This is connected to the gas supply by means of a short piece of rubber tubing.

After slipping the upper end of the rubber tubing securely over the jet of the H_2S supply, turn on the gas. Loosen the stopper in the flask for a moment so as to displace the air, and then press it back firmly into place. Occasional shaking will hasten precipitation.

If by too violent shaking some of the solution should be thrown against the stopper and the glass tube, they should be thoroughly cleaned before being used again.

Never bubble H_2S through a solution in an open vessel. Such practice not only vitiates the air in the room and sometimes spoils results in other experiments, but it is dangerous. *H_2S is poisonous.*

Note.—H_2S is a very sensitive test for the presence of Ag compounds. If AgCl were appreciably soluble in water, a brown color or precipitate would appear at this point.

(2) **Group II.**—Use $Hg(NO_3)_2$ solution as representative of this group. Take 2 cc. of this solution and dilute to 40 cc. in an Erlenmeyer flask. Add dilute HCl as in the preceding experiment (?). Saturate the solution with H_2S, warm,[1] and filter. After proving that the precipitation is complete by adding an equal volume of water and saturating again with H_2S, add to the filtrate NH_4OH to alkalinity (litmus test), and saturate with H_2S (?).

(3) **Group III.**—Use $Zn(NO_3)_2$ solution as representative of this group. Take 2 cc. of this solution and dilute to 100 cc. Now add 4 cc. of dilute HCl (?). Saturate this acid solution with H_2S (?). Now add NH_4OH until, after the mixture has been shaken, a drop of it on a stirring rod will turn red litmus paper blue. Saturate again with H_2S (?). After testing for the completeness of the precipitation, add $(NH_4)_2CO_3$ solution to the filtrate (?).

(4) **Group IV.**—Use $Ca(NO_3)_2$ solution as representative of this group. Take 2 cc. of this solution and dilute it to 40 cc. Add 4 cc. of dilute HCl (?), saturate with H_2S (?), add NH_4OH in excess (litmus test) and pass in H_2S again (?), add $(NH_4)_2CO_3$ solution (?). If a precipitate does not form at once, heat just to boiling and allow to stand half an hour.

(5) **Group V.**—Use $Mg(NO_3)_2$ solution as representative of this group. Take 2 cc. of this solution and dilute to 40 cc. Add 4 cc. of dilute HCl (?), saturate with H_2S (?), add NH_4OH in excess (litmus test) and pass in H_2S again (?), add $(NH_4)_2CO_3$ solution (?). Define Group V (?). To some diluted $Mg(NO_3)_2$ solution add Na_2CO_3 solution (?). Would it be correct to state that magnesium carbonate is soluble in water?

(6) **Effect of Incomplete Precipitation.**—Try the following experiments: $AgNO_3$ solution + H_2S (?), $Hg(NO_3)_2$ solution + NH_4OH + H_2S (?), $Zn(NO_3)_2$ solution + $(NH_4)_2CO_3$ solution (?). What would be the effect if each of these cations were not completely precipitated in its own group?

[1] Heat helps to coagulate a number of precipitates, making them more easily filtered.

Exercises[1]

1. Name the group reagent for each of the first four cation groups.
2. What is a test for completeness of precipitation?
3. Name three solutions besides HCl that might be used to precipitate AgCl from $AgNO_3$ solution.
4. A student reported Groups III and IV in a "group unknown" containing only $Zn(NO_3)_2$. Point out the error in his technique.
5. Suppose four portions of a "group unknown" are tested, each by one of the group reagents. If the unknown contained mercurous nitrate, $Hg_2(NO_3)_2$, what groups would be reported? (In case of uncertainty, try these tests.)
6. Fill in the blanks in the following sentences with the proper word, "soluble" or "insoluble":

   AgCl is.....in water.
   HgS is.....in water,.....in dilute acids.
   ZnS is.....in water,.....in dilute acids,
   .....in NH_4OH.
   $CaCO_3$ is.....in water,.....in water containing ammonium salts.
   $MgCO_3$ is.....in water,.....in water containing ammonium salts.
   All nitrates in the above experiments appear to be.....in water.

7. What is the meaning of the following symbols used in this book: (?), (E), (R), (Instructions)?

ANALYSIS

(7) Group I.—Take 3 or 4 cc. of the solution to be analyzed and dilute with about 10 cc. of distilled water. Disregard any precipitate that may form during the dilution. Add 4 cc. of dilute HCl, or such amount as may be necessary to complete the precipitation. A precipitate insoluble in dilute HCl indicates what group? Shake well, filter, and wash[2] the precipitate, first with 1 cc. of dilute HCl diluted to 4 cc., and then with cold

[1] The exercises at the end of each set of preliminary experiments are easy, and the student who has performed his work faithfully and intelligently should have no trouble with them. It is suggested that the student should be able to answer such questions as these in an informal laboratory quiz by the instructor before an "unknown" is issued for analysis. They should also be helpful in review and test exercises.

[2] The precipitate on the filter paper should be washed down towards the apex of the funnel by a fine stream of water from the wash bottle, played first on the upper edges of the paper and then downward. Only a small amount of water should be used at a time, and this should be allowed to run through completely before more is added.

water (using portions of about 5 cc.), adding the washings to the filtrate. Reserve the filtrate for (**8**).

(**8**) **Group II.**—Dilute the filtrate from (**7**) (which now contains 4 cc. of dilute HCl or its equivalent of other acids) to 100 cc. and saturate with H_2S. A precipitate indicates what group? Heat nearly to boiling and filter. Wash with a little warm water, and reserve the filtrate for (**9**).

(**9**) **Group III.**—To the acid filtrate from (**8**) add NH_4OH to alkaline reaction (litmus test) and saturate with H_2S. A precipitate indicates what group? Filter and wash, reserving filtrate for (**10**).

(**10**) **Group IV.**—Acidify the filtrate from (**9**) with dilute HCl and concentrate to 25 or 30 cc. by boiling in an open beaker.[1] Filter, if a precipitate (sulfur) appears. Add NH_4OH to alkaline reaction. Heat to boiling and add $(NH_4)_2CO_3$ until precipitation is complete. In case of doubt, let the mixture stand 15 minutes before deciding that no precipitate has formed. A precipitate indicates what group?

Group V.—Since there is no group reagent for Group V, no further tests need be made, and no report on the presence or absence of this group need be given.

TABLE I.—SEPARATION OF CATION GROUPS

(**7**)[2] Dilute the unknown solution with 10 cc. of water and add dilute HCl (about 4 cc., usually). Filter, wash precipitate.

Precipitate: Group I (as chlorides) See Table II	(**8**) Filtrate: Dilute to 100 cc. and saturate with H_2S. Filter, wash precipitate.	
	Precipitate: Group II (as sulfides) See Table III	(**9**) Filtrate: Add $NH_4OH + H_2S$. Filter, wash precipitate.
		Precipitate: Group III (as sulfides and hydroxides) See Table VI
		(**10**) Filtrate: Add $(NH_4)_2CO_3$ Filter, wash precipitate.
		Precipitate: Group IV (as carbonates) See Table XI
		Filtrate: Group V See Table XIII

[1] Start (**11**), (**12**), and (**13**) while this evaporation is in progress.

[2] The numbers in parentheses refer to the corresponding paragraphs under the detailed analytical procedure.

GROUP I. THE HYDROCHLORIC ACID GROUP

This group contains the cations, Pb^{++}, Ag^{+}, and Hg_2^{++}. The group characteristic is that the chlorides of these cations are, with the exception of $PbCl_2$, insoluble in water and in dilute HCl. $PbCl_2$ is slightly soluble in cold water, and readily soluble in hot water. As a result, the Pb^{++} ion is not completely precipitated in this group, but appears also in Group II. If it is present in the solution in small quantity only, it may not be found at all in Group I, but wholly in Group II.[1]

PRELIMINARY EXPERIMENTS

(**11**) **Lead, Pb^{++}.** 1. *Solubility of Lead Chloride.*—Take 2 cc. of a solution of lead nitrate, $Pb(NO_3)_2$, dilute to 10 cc., and add dilute HCl slowly, with shaking, as long as the amount of precipitate appears to increase (E).[2] Allow the precipitate to settle, and decant[3] the clear liquid. Add about 10 cc. of water to the precipitate and boil. If the precipitate does not dissolve completely, decant the liquid into a test tube, add more water, and boil again. Repeat until solution is complete. Save the solution for the next experiment.

2. *Precipitation of Lead Chromate.*—Add to a portion of the hot solution from (**11**, 1) a few drops of potassium dichromate solution, $K_2Cr_2O_7$. The yellow precipitate is lead chromate, $PbCrO_4$ (E). Try the reaction of the mixture on blue litmus paper (?). Account for the strongly acid reaction (?).

[1] Lead chloride is freely soluble in solutions containing tartrates, acetates, and a number of other anions, so that in the presence of excess of these anions Pb^{++} will probably be found in Group II only.

[2] In writing equations, always write below the formula of a new substance its name and its most important properties; *e.g.*,

$$Pb(NO_3)_2 + 2HCl \rightarrow \underset{\substack{\text{Lead Chloride.}\\ \text{White, soluble}\\ \text{in hot } H_2O.}}{PbCl_2} + 2HNO_3.$$

[3] Heavy precipitates are readily washed by decantation (see page xi). The precipitate is allowed to settle, and the supernatant liquid is poured off, best through a filter, so as to lose none of the solid. Water is then added, the mixture well stirred and allowed to stand until the precipitate has settled, and the supernatant liquid again poured off. This process may be repeated as many times as necessary.

(12) Silver, Ag^+. 1. *Insolubility of Silver Chloride in Water.*—Take 2 cc. of $AgNO_3$ solution, dilute to about 10 cc., and add dilute HCl, with vigorous shaking, until precipitation is complete (E). Decant, as in **(11)**. Try the solubility of AgCl in hot water by boiling the precipitate with water, filtering, and testing the filtrate for Ag^+ by H_2S. (SEPARATION OF Ag^+ FROM Pb^{++}.) Is AgCl soluble in water? Save the residue for the next experiment.

2. *The Silver-ammonia Complex.*—Dissolve the AgCl from the preceding experiment in a little NH_4OH (E). The Ag^+ combines with the NH_3 of the NH_4OH to give $Ag(NH_3)_2^+$. Acidify this ammoniacal solution with dilute HNO_3 (?, E).

(13) Mercurous Mercury, Hg_2^{++}. 1. *Properties of Mercurous Chloride.*—Take 2 cc. of mercurous nitrate solution, $Hg_2(NO_3)_2$, dilute to 10 cc., and add dilute HCl until precipitation is complete (E). Filter, and wash the precipitate three times with cold water, using portions of about 10 cc., to remove mercuric[1] salts. Now wash with 10 cc. of boiling water, and test the filtrate for Hg_2^{++} with H_2S (?). Reserve the residue on the filter paper for the next experiment.

2. *Reaction of Mercurous Chloride with Ammonia.*—Pour NH_4OH over the residue from the preceding experiment (?). The product consists of a mixture of $HgNH_2Cl + Hg$ (E). (SEPARATION OF Hg_2^{++} FROM Ag^+.)

Exercises

1. Criticize the following definition of Group I: "Group I consists of the metals insoluble in dilute HCl."
2. Point out a case of physical solution and one of chemical solution in the preliminary experiments on Group I. Which one of these may be represented by an equation?
3. Fill in the blanks in the following table by the words "soluble" or "insoluble":

	HOT WATER	NH_4OH
Lead chloride	.....	.....
Silver chloride	.....	.....
Mercurous chloride	.....	.....

4. What ion of Group I forms a chloride appreciably soluble in cold water?

[1] Solutions of mercurous salts usually contain mercuric salts, owing to the ready oxidation of the former by the oxygen of the air.

5. Lead chloride is easily soluble in solutions containing acetates. Suppose a solution consisting of $Pb(NO_3)_2$ and excess of $NaC_2H_3O_2$ solutions. In what group would Pb^{++} be found?
6. Point out the possible errors in technique when $PbCl_2$ is present in the HCl precipitate, and yet is not found by the $K_2Cr_2O_7$ test.
7. What would be the result if, in analyzing a solution containing $AgNO_3$ and $Ba(NO_3)_2$, the AgCl precipitate was not thoroughly washed? Remember that $BaCrO_4$ is yellow and insoluble in $HC_2H_3O_2$.
8. In which case is it easier to see a yellow precipitate, when it is suspended in an orange liquid or in a colorless one? In the confirmatory test for Pb^{++}, should the $K_2Cr_2O_7$ solution be added in excess, or only 1 or 2 drops?
9. What reagents besides HNO_3 might be used to precipitate AgCl from a solution containing $Ag(NH_3)_2Cl$?
10. What is a usual impurity in mercurous salt solutions?
11. Criticize the following equation: $Hg_2Cl_2 + NH_4OH$ (excess) $\rightarrow HgNH_2Cl + Hg + HCl + H_2O$.
12. Dilute HCl is added to a hot solution of a Group I unknown without effect; a white precipitate, however, forms on cooling. What members of the group may be present?
13. A solution gives with dilute HCl a white precipitate insoluble in hot water and insoluble in NH_4OH, but blackened by the latter. Interpret.

ANALYSIS

(**14**) **Precipitation.**—Dilute the solution[1] (a 3- or 4-cc. portion of the solutions issued as "unknowns"[2] is generally sufficient for an analysis) in a small beaker or Erlenmeyer flask with about 10 cc. of water, and add 4 cc. of dilute HCl. If no precipitate is formed, Group I is absent; proceed to (**26**). If a precipitate is formed, stir well, and let the mixture stand until the precipitate has settled. Add a drop or two of dilute HCl to the clear liquid above the precipitate. If no further precipitate forms, the precipitation is known to be complete. If a precipitate is formed, more HCl must be added until repetition of the test shows that precipitation is complete. Dilute the mixture to about 25 cc.

Note.—The volume of HCl used is important in order that the acid concentration of the filtrate may be suitable for the precipitation of Group II

[1] If the solution contains a precipitate, see Part III, "Systematic Analysis," page 109.

[2] The solutions issued as "unknowns" to beginners should be neutral or only slightly acid. (See page 109 for procedure in the case of alkaline solutions.)

by H_2S. If more than 5 cc. of dilute HCl are used, the acid concentration must be adjusted by (**26**) in order to precipitate Group II completely.

Allow the precipitate to settle, and decant the supernatant liquid through a filter, leaving the precipitate in the beaker as far as possible. Wash the residue, first with 1 cc. of dilute HCl, to which has been added 3 or 4 cc. of water, and then with 5 cc. of cold water, decanting through the filter as before. Combine all the filtrates and reserve for (**26**). Analyze the precipitate by (**15**), (**16**), and (**17**).

Note.—The purpose of the washing with dilute HCl is to remove BiOCl and SbOCl, which are insoluble in water.

(**15**) **Lead.**—Add 10 cc. of water to the residue in the beaker and bring to a boil, decanting through the same filter as before, but receiving the washings in a fresh test tube. To this filtrate add a single drop of $K_2Cr_2O_7$ solution. A yellow precipitate of $PbCrO_4$ indicates Pb^{++}.

Notes.—1. $PbCl_2$ dissolves slowly. For this reason it is most readily brought into solution by boiling with water, rather than by simply pouring hot water over the precipitate on the filter paper.

2. In the precipitation of $PbCrO_4$, an excess of $K_2Cr_2O_7$ solution is avoided, since many students have trouble in seeing a yellow precipitate in an orange solution.

(**16**) **Silver.**—If Pb^{++} has been found, boil the residue with a fresh amount of water, and decant as before. Continue this extraction until a fresh sample of the filtrate fails to give a precipitate with $K_2Cr_2O_7$ solution. Then add 5 to 10 cc. of NH_4OH to the residue and pour through the filter several times. Acidify this ammoniacal solution with dilute HNO_3. (Use litmus test!) A curdy white precipitate indicates Ag^+.

(**17**) **Mercurous Mercury.**—If the residue in the beaker and on the paper blackens during the NH_4OH treatment, the presence of Hg_2^{++} is indicated.

Note.—The black precipitate, $HgNH_2Cl + Hg$, has the property of preventing NH_4OH from completely dissolving the AgCl from a mixture of Hg_2Cl_2 and AgCl. In case of a large excess of Hg_2Cl_2 and a small amount of AgCl, the test for Ag^+ in (**16**) may be negative. In such cases traces of Ag^+ may be detected in the following way:

Silver in the Mercury Residue.[1]—Pour hot dilute aqua regia (prepared by mixing 3 volumes of dilute HCl and 1 volume of dilute HNO_3 and boiling) through the paper in the funnel, converting the Hg into soluble $HgCl_2$ and the Ag into insoluble AgCl. After washing with warm water to remove the $HgCl_2$, NH_4OH is poured through the paper, and the test for Ag^+ is made as in (16).

Note.—The failure of the NH_4OH to separate Ag from the black Hg residue is due to the fact that Ag^+ has been converted by the free Hg into metallic Ag, which is insoluble in NH_4OH. The equation for this action is $2AgCl + 2Hg \rightleftarrows 2Ag + Hg_2Cl_2$. This reaction is theoretically reversible, but in this case it goes to practical completion to the right, owing to the removal of the Hg_2Cl_2, which is converted by the NH_4OH into $HgNH_2Cl + Hg$.

TABLE II.—ANALYSIS OF GROUP I

(14) Solution: Neutral or slightly acid solution, containing Group I and perhaps subsequent groups. Add dilute HCl and dilute to 40 cc. Filter, and wash the precipitate, first with a little dilute HCl, and then with cold water.

<table>
<tr><td colspan="2">Precipitate: $PbCl_2$, AgCl, Hg_2Cl_2. (15) Extract the precipitate with hot water.</td><td rowspan="2">Filtrate: Groups II, III, IV, V. See Table III.</td></tr>
<tr><td>Solution: $PbCl_2$. Add $K_2Cr_2O_7$. Precipitate: Yellow $PbCrO_4$.</td><td>Residue: AgCl, Hg_2Cl_2. (16) Extract with NH_4OH.
Filtrate: $Ag(NH_3)_2Cl$. Add dilute HNO_3. Precipitate: White AgCl. | (17) Residue: Black $HgNH_2Cl + Hg$.</td></tr>
</table>

GROUP II. THE HYDROGEN SULFIDE GROUP

This group contains the cations, Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, Sn^{++} and Sn^{++++}, As^{+++} and As^{+++++}, and Sb^{+++}. These cations form chlorides soluble in water or dilute acids, and with H_2S form sulfides insoluble in water and in dilute acids. It is divided into two subgroups on the basis of the solubility of the sulfides of these cations in ammonium polysulfide, $(NH_4)_2S_x$:

[1] This procedure may be omitted in elementary courses.

(*a*) The Copper Subgroup, whose sulfides are insoluble,[1] including Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, and Cd^{++}.

(*b*) The Tin Subgroup, whose sulfides are soluble, containing Sn^{++} and Sn^{++++}, As^{+++} and As^{+++++}, and Sb^{+++}.

PRELIMINARY EXPERIMENTS

(18) Mercuric Mercury, Hg^{++}. 1. *Precipitation and Solubility of Mercuric Sulfide.*—Take 2 cc. of mercuric chloride solution, $HgCl_2$, add 4 cc. of dilute HCl, and dilute to 40 cc. Saturate with H_2S (E), noting changes in the color of the precipitate formed (?). Warm (to hasten coagulation), wash three or four times by decantation, and filter. Divide the precipitate into two parts. Try the solubility of one part by boiling for a minute in dilute HNO_3 (made by adding 2 volumes of water to 1 volume of ordinary dilute HNO_3) (?). (SEPARATION OF HgS FROM PbS, Bi_2S_3, CuS, CdS.) Try the solubility of the other part in aqua regia (formed by mixing 3 volumes of concentrated HCl with 1 volume of concentrated HNO_3 and heating) (E).

Notes.—1. The precipitate formed by H_2S with a solution of $HgCl_2$ shows the following succession of colors: white, yellow, brown, black. The black substance is HgS. The others are mixed salts, intermediate in composition between $HgCl_2$ and HgS; *e.g.*, $HgCl_2.2HgS$ (white).

2. The insolubility of HgS in hot dilute HNO_3 is due to its extremely low solubility in water; that is, it is only the dissolved portion that reacts with the solvent acid. HgS is by far the most insoluble sulfide of the Copper Subgroup.

3. Prolonged boiling of the dilute HNO_3 will concentrate it somewhat, and the HgS will be changed first into the insoluble $Hg(NO_3)_2.2HgS$, and later into the soluble $Hg(NO_3)_2$.

4. Aqua regia is made, as stated above, by mixing 3 volumes of HCl with 1 volume of HNO_3, and heating. Free chlorine is formed, the equation being approximately written: $3HCl + HNO_3 \rightarrow 3Cl + 2H_2O + NO$. The chlorine is in an extremely active form, known as the "nascent state." In the opinion of many, the molecules of nascent chlorine consist of single atoms, and the high reactivity is attributed to the free valences.

5. The solubility of HgS in aqua regia, but not in HNO_3, depends upon the fact that aqua regia is a more active oxidizing agent for the S^{--} ion than HNO_3 is. That is to say, the concentration of the S^{--} ion in saturated HgS solution is large enough to react with aqua regia, but too small to react with dilute HNO_3. The S^{--} ion may be considered as being oxidized by the nascent chlorine in aqua regia, thus: $S^{--} + 2Cl \rightarrow S + 2Cl^-$. The low

[1] CuS is slightly soluble, and HgS to a still smaller extent, in $(NH_4)_2S_x$.

ionization of the $HgCl_2$ formed may have something to do with the completeness of the reaction.

2. *Reduction of Mercuric Chloride by Stannous Chloride.*—Dilute 2 cc. of $HgCl_2$ solution to 5 cc., and add 1 or 2 drops of stannous chloride solution, $SnCl_2$, and shake promptly (?, E). Now dilute 2 cc. of $SnCl_2$ solution and add $HgCl_2$ solution drop by drop (?, E). Write the colors under the formulas of the precipitates in the equations. Note that the product in the reaction between $HgCl_2$ and $SnCl_2$ solutions depends on the relative amounts of these substances.

Note.—The reduction of $HgCl_2$ by $SnCl_2$ may be represented as proceeding in stages, thus:

(1) $2HgCl_2$ (excess) + $SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
(2) $Hg_2Cl_2 + SnCl_2$ (excess) $\rightarrow 2Hg + SnCl_4$.

(19) Lead, Pb^{++}. 1. *Precipitation and Solubility of Lead Sulfide.*—Take 10 cc. of lead chloride solution, $PbCl_2$, add 4 cc. of dilute HCl, dilute to 40 cc., warm, and saturate with H_2S (E). Wash the precipitate by decantation and test its solubility in boiling dilute HNO_3 (prepared by adding 2 volumes of water to 1 volume of ordinary dilute HNO_3) (E). (Separation of PbS from HgS.)

2. *Conversion of Lead Nitrate into Lead Sulfate.*—To 1 cc. of lead nitrate solution, $Pb(NO_3)_2$, add 5 cc. of dilute H_2SO_4 and evaporate (E) in a small Pyrex[1] beaker until heavy white fumes of SO_3 begin to come off. (Do not mistake the lighter HNO_3 fumes for SO_3. The latter may be recognized [Be cautious!] by their producing involuntary fits of coughing.) After cooling (*Important!* What is the danger?) pour into 10 or 15 cc. of cold water, rinsing the beaker with a little of the diluted solution. Is $PbSO_4$ soluble in dilute H_2SO_4? (Separation of Pb^{++}

[1] Pyrex is a high-melting glass approaching quartz in its composition and properties. Pyrex vessels are recommended for use in Qualitative Analysis instead of porcelain for two reasons: (1) Pyrex is much more resistant to attack by chemical reagents than porcelain, which is apt to contaminate a solution by introducing Al^{+++} ions, especially after the glaze has been destroyed by contact with alkalies; (2) Pyrex has a very low coefficient of expansion, so that there is not so much probability of breakage upon evaporating a solution to dryness, or upon adding cold water to a hot vessel of this material.

FROM Bi^{+++}, Cu^{++}, Cd^{++}.) Allow the precipitate to settle and pour off the clear liquid. Add to the residue 10 cc. of 10 per cent ammonium acetate solution, $NH_4C_2H_3O_2$, and warm, shaking frequently, until solution is complete (E). Add to the solution 1 or 2 drops of potassium dichromate solution, $K_2Cr_2O_7$ (E), and then make the solution strongly acid with acetic acid, $HC_2H_3O_2$ (3 or 4 cc.). Is $PbCrO_4$ soluble in $HC_2H_3O_2$?

Notes.—1. The insoluble residue left when dilute HNO_3 acts on a sulfide is sulfur. It is frequently colored by the inclusion of small amounts of undissolved sulfide.

2. H_2S is not given off when HNO_3 reacts with sulfides. Recall that H_2S is an active reducing agent, and will react with HNO_3 forming H_2O, S, and NO, thus: $3H_2S + 2HNO_3 \rightarrow 4H_2O + 3S + 2NO$.

3. The evaporation with H_2SO_4 is necessary to expel the free HNO_3. $PbSO_4$ is somewhat soluble in HNO_3, owing to the reversibility of the reaction, $Pb(NO_3)_2 + H_2SO_4 \rightleftarrows PbSO_4 + 2HNO_3$. Of the four substances in this equation, HNO_3 has the lowest boiling point, and consequently it is the first to be vaporized. Its loss shifts the equilibrium to the right of the equation as here written, converting the Pb^{++} completely into the insoluble $PbSO_4$.

4. The solvent action of $NH_4C_2H_3O_2$ on $PbSO_4$ is explained as due to the stability (*i.e.*, the low ionization) of $Pb(C_2H_3O_2)_2$. It would appear that $PbSO_4$, although only slightly soluble, is soluble enough to furnish a higher concentration of Pb^{++} ions than does the soluble $Pb(C_2H_3O_2)_2$. The equilibrium may be formulated thus:

$$\left.\begin{array}{l} 2NH_4C_2H_3O_2 \rightleftarrows 2NH_4^+ + 2C_2H_3O_2^- \\ PbSO_4 \rightleftarrows SO_4^{--} + Pb^{++} \end{array}\right\} \begin{array}{c}\longrightarrow \\ \leftarrow\end{array} Pb(C_2H_3O_2)_2.$$

$$\uparrow\downarrow$$

$$\underline{PbSO_4}$$

5. The insolubility of $PbCrO_4$ in $HC_2H_3O_2$ serves to distinguish it from bismuthyl dichromate, $(BiO)_2Cr_2O_7$, which is formed when $K_2Cr_2O_7$ solution is added to a solution of a Bi^{+++} salt in the absence of acids.

(20) Bismuth, Bi^{+++}. 1. *Hydrolysis of Bismuth Salts.*—To 2 cc. of bismuth nitrate solution, $Bi(NO_3)_3$, in a test tube add a few cubic centimeters of water (?, E). How could it be shown that the reaction is reversible?

Note.—Bismuth salts on hydrolysis form basic salts containing the bismuthyl radical, BiO^+; *e.g.*, $BiONO_3$, called "bismuthyl nitrate" or "bismuth oxynitrate." This salt may be considered as formed from the basic salt, $Bi(OH)_2NO_3$, by the loss of 1 molecule of water.

2. *Precipitation of Bismuth Sulfide.*—Take 2 cc. of $Bi(NO_3)_3$ solution[1] and dilute to 40 cc. This may cause a precipitation of bismuthyl nitrate, $BiONO_3$. Whether a precipitate forms or not, warm and saturate with H_2S. Write the equation for the reaction of H_2S with $Bi(NO_3)_3$ (E). What is the color of Bi_2S_3? Write the equation for its solution in hot dilute HNO_3 (E).

3. *Formation and Hydrolysis of Bismuth Sulfate.*—What would be the result (the actual experiment may be omitted) of evaporating $Bi(NO_3)_3$ solution with excess of H_2SO_4(E)? If $Bi_2(SO_4)_3$ were diluted with water (E)?

4. *Precipitation of Bismuth Hydroxide.*—To a little $Bi(NO_3)_3$ solution add NH_4OH (E). Is $Bi(OH)_3$ soluble in excess of the reagent? (SEPARATION OF Bi^{+++} FROM Cu^{++} AND Cd^{++}.) Save the mixture for the next test.

5. *Reduction of Bismuth Hydroxide by Sodium Stannite.*—Filter the $Bi(OH)_3$ from the preceding experiment, and pour over it on the filter a little freshly prepared sodium stannite solution, Na_2SnO_2.[2] A black residue is metallic Bi (E).

Notes.—1. $BiONO_3$ is slightly soluble in water, and gives a much higher concentration of Bi^{+++} than does Bi_2S_3. Consequently, H_2S readily converts the precipitate $BiONO_3$ into Bi_2S_3.

2. In every reduction reaction there is also oxidation. In the reaction between $Bi(OH)_3$ and Na_2SnO_2, the Bi^{+++} is reduced to Bi; and the Na_2SnO_2, containing Sn^{II}, is oxidized to Na_2SnO_3, containing Sn^{IV}.

(21) Copper, Cu^{++}. 1. *Precipitation of Copper Sulfide.*—Take 2 cc. of cupric nitrate solution, $Cu(NO_3)_2$, add 4 cc. of dilute HCl, dilute to 40 cc., warm and saturate with H_2S (E). What is the color of CuS? Write the equation for its solution in dilute HNO_3 (E).

2. *Evaporation of Cupric Nitrate Solution with Sulfuric Acid.*—Write the equation for the conversion of $Cu(NO_3)_2$ into $CuSO_4$, specifying the condition for making the reaction complete (E, ?).

3. *Reaction with Ammonia.*—Add 1 or 2 cc. of $Cu(NO_3)_2$ solution to 5 cc. of water, add NH_4OH, at first drop by drop

[1] $Bi(NO_3)_3$ solution contains a considerable amount of free HNO_3 to prevent the formation of a precipitate of $BiONO_3$.

[2] Na_2SnO_2 solution is made by adding excess of NaOH solution to $SnCl_2$ solution slowly, with shaking, until a white precipitate of $Sn(OH)_2$ fails to form upon adding a few drops more of the base. Add to the mixture an equal volume of water.

(?, E), and then in excess (E). (SEPARATION OF Cu^{++} FROM Bi^{+++}.) The blue color of the final solution is due to the complex ion, $Cu(NH_3)_4^{++}$. Reserve this solution for (**21,** 4) below.

Note.—Since the sparingly soluble $Cu(OH)_2$ dissolves so readily in NH_4OH to form the soluble $Cu(NH_3)_4^{++}$, it follows that the former must furnish a considerably higher concentration of Cu^{++} ions than the latter.

4. *The Ferrocyanide Reaction.*—Transfer a very little of the deep-blue solution formed in the preceding experiment to a beaker and add water until the color is faint and indecisive. Now acidify a 5-cc. sample of this dilute solution with dilute H_2SO_4 (E) and add a single drop of potassium ferrocyanide solution, $K_4Fe(CN)_6$ (E). The rose color is due to $Cu_2Fe(CN)_6$.

5. *Displacement of Copper by Iron.*—Place 2 or 3 cc. of cupric sulfate solution, $CuSO_4$, in a beaker, add about 50 cc. of water and about 1 cc. of Fe filings, cover with a watch glass, and boil gently until the blue color of the Cu^{++} has completely disappeared (E). Filter and test the filtrate for Cu^{++} by adding dilute HCl and saturating with H_2S (?). (SEPARATION OF Cu^{++} FROM Cd^{++}.) Name two other metals that would displace Cu^{++} in a similar way (?). (See Appendix, page 126.)

*6. *Formation of the Cyanide Complex.*[1]—To a few drops of $CuSO_4$ solution in a H_2S precipitation flask add about 40 cc. of water, and then NH_4OH until the deep-blue solution is obtained. Now add NaCN solution slowly until the blue color is bleached out, and then saturate with H_2S (?) Which gives the higher copper ion concentration, Cu_2S or $Cu(CN)_2^-$?

Note.—Copper compounds react with NaCN forming cuprocyanides, which show few of the characteristic properties of Cu^{++} or Cu_2^{++}. The equations involved in the above reactions are:

$$CuSO_4 + 2NaCN \rightarrow Cu(CN)_2 \text{ (unstable)} + Na_2SO_4$$
$$2Cu(CN)_2 \rightarrow 2CuCN + C_2N_2 \text{ (gas)}$$
$$CuCN + NaCN \rightarrow NaCu(CN)_2.$$

$NaCu(CN)_2$ ionizes, giving Na^+ and the very stable complex anion, $Cu(CN)_2^-$.

* Experiments and procedures marked with an asterisk * may be omitted at the discretion of the instructor. They are always alternative procedures, as in this case, or else tests or methods required in special or advanced analyses only. The student should consult with his instructor in all such cases.

[1] On account of the exceedingly poisonous nature of cyanides, it is recommended that this experiment be omitted by beginning students.

(22) **Cadmium, Cd^{++}.** 1. *Precipitation of Cadmium Sulfide.*—Take 5 cc. of cadmium nitrate solution, $Cd(NO_3)_2$, add 4 cc. of dilute HCl, and dilute to 40 cc. Place in an Erlenmeyer flask, heat nearly to boiling, and saturate while hot with H_2S (E), wrapping a towel around the flask to prevent loss of heat. Filter while still hot and ascertain if the precipitation is complete by cooling and diluting to 100 cc. and passing H_2S into the cold solution (?).

Is there any difference in the color of the precipitates formed from the hot and cold solutions? What are the best conditions for the complete precipitation of Cd^{++} as CdS?

Note.—The orange color of CdS precipitated from hot solution is due to a mixed salt of the composition $CdCl_2.CdS$. In the cold, yellow CdS is formed.

2. *Reaction with Ammonia.*—Dilute 2 cc. of $Cd(NO_3)_2$ solution to about 5 cc. and add NH_4OH drop by drop (E), and then in excess (E). Compare with the reaction between $Cu(NO_3)_2$ and NH_4OH, and write analogous equations.

3. *Displacement.*—Would Cd^{++} be displaced from solution by Fe, as in the case of Cu^{++}? See "Electromotive Series," page 126.

*4. *Decomposition of the Cyanide Complex by Hydrogen Sulfide.*[1] Place a little $Cd(NO_3)_2$ solution in a precipitation flask, dilute to about 40 cc., and add excess of NH_4OH to convert it into the complex ion, $Cd(NH_3)_4^{++}$. Now add NaCN solution and saturate with H_2S (?). Which gives the higher Cd^{++}-ion concentration, $Cd(CN)_4^{--}$ or CdS? Compare results with (**21,** 6) above.

Note.—When NaCN solution is added to a solution of a Cd^{++} salt, a white precipitate of $Cd(CN)_2$ at first forms, but later redissolves in the excess NaCN, forming $Na_2Cd(CN)_4$. This complex salt dissociates mainly into Na^+ and $Cd(CN)_4^{--}$; the latter, however, dissociates further to a certain extent into Cd^{++} and CN^-.

(23) **Stannous Tin, Sn^{++}, and Stannic Tin, Sn^{++++}.** 1. *Sulfides.*—Dilute a 2-cc. sample of stannous chloride solution,[2]

[1] To be omitted by elementary students.

[2] $SnCl_2$ and $SnCl_4$ always contain considerable amounts of free acid to prevent hydrolysis. The precipitation of the sulfides in this experiment therefore takes place in acid solution, as in the case of the other members of Group II.

$SnCl_2$, to about 50 cc. and saturate with H_2S (E). Treat a sample of stannic chloride solution, $SnCl_4$, in a similar way (E). Write the color beneath the formula of the precipitate in the two equations. Filter, and suspend portions of each precipitate in NH_4OH and saturate with H_2S[1] (E). Which one fails to dissolve in colorless ammonium sulfide, $(NH_4)_2S$? To the unchanged mixture add a few drops of yellow ammonium sulfide, $(NH_4)_2S_x$, and warm (?, E). Now acidify the resultant solution with dilute HCl (E). Account for the color of the precipitate (?).

Dilute 2 cc. of $SnCl_4$ solution to about 25 cc., place in a precipitation flask, and add NH_4OH until a permanent precipitate forms, so as to neutralize the free acid present. Add 10 cc. of saturated oxalic acid solution, $H_2C_2O_4$, warm, and saturate with H_2S (?).

Note.—The failure of SnS_2 to precipitate in concentrated oxalic acid solution is the basis of a separation of Sn^{IV} from As^{V} and Sb^{V}, both of which are precipitated completely as sulfides by H_2S in the presence of this acid.

2. *Displacement of Tin by Aluminium.*—Dilute 1 cc. of $SnCl_4$ solution to about 10 cc., add 5 cc. of dilute HCl and a small piece of metallic aluminium. Warm, if necessary, to start the reaction. What is the mouse-colored precipitate which collects on the Al (E)? After the reaction becomes slow, heat to boiling until the Sn is completely redissolved (E). Filter the liquid into 5 cc. of mercuric chloride solution, $HgCl_2$, in a test tube (?, E).

If metallic Al were added to a solution of $AsCl_3$ or $SbCl_3$, which stage of the above reaction would be lacking? Compare the positions of Sn, As, and Sb in the Electromotive Series with respect to H (?). (SEPARATION OF Sn^{++} FROM As^{+++} AND Sb^{+++}.) (See Appendix, page 126.)

3. *Reducing Action of Stannous Chloride.*—Recall the reaction between $HgCl_2$ and $SnCl_2$ solutions (two stages) (E's). How is the valence of an element effected by (*a*) oxidation, (*b*) reduction?

[1] Saturation of NH_4OH with H_2S gives colorless ammonium sulfide, $(NH_4)_2S$, thus: $2NH_4OH + H_2S \rightarrow (NH_4)_2S + 2H_2O$. Upon boiling colorless ammonium sulfide with sulfur, yellow ammonium sulfide (also called "ammonium polysulfide") is formed, thus: $(NH_4)_2S + (x-1)S \rightarrow (NH_4)_2S_x$.

4. *Metastannic Acid.*—Place a piece of metallic Sn in a small beaker or dish, add 5 or 10 cc. of concentrated HNO_3, and warm as long as brown fumes are given off (E). Consider the precipitate $SnO_2.xH_2O$. Allow the precipitate to settle and decant the liquid. Try to dissolve a portion of the residue in dilute HCl (?). Now add to the HCl-SnO_2 mixture an equal volume of water and a piece of Al wire, and warm. After the Al is completely dissolved, boil for 2 or 3 minutes to redissolve any Sn that may have separated (see (**23**, 2)), and filter into $HgCl_2$ solution (?).

Note.—This procedure is very useful in testing insoluble precipitates for Sn. See pages 23, 111.

(24) Arsenic: Arsenious, As^{+++}, and Arsenic, As^{+++++}. 1. *Precipitation of Arsenic Trisulfide from Arsenious Compounds.*—Dilute 2 cc. of arsenic trichloride solution,[1] $AsCl_3$, to 40 cc. and saturate with H_2S (E). Does the precipitate form immediately?

2. *Precipitation of Arsenic Pentasulfide from Arsenates.*—Take 2 cc. of potassium arsenate solution, K_3AsO_4, dilute to 40 cc., and divide into three parts. Saturate one of these parts cold with H_2S (?).

Heat a second portion nearly to boiling, add 2 or 3 cc. of concentrated HCl, and pass H_2S into the hot solution.[2] Does the precipitate form more rapidly than in the preceding experiment?

Treat the third portion exactly as the second, only add 1 cc. of NH_4I solution just before passing the H_2S. The As in this case is precipitated almost wholly as As_2S_3. Save for (**24**, 3), below.

Is there any difference in the speed of precipitation in the three cases? State concisely the most favorable conditions for the precipitation of arsenic sulfide from arsenates (?).

Note.—The action of NH_4I in hastening the precipitation of arsenic sulfide from arsenates depends on the fact that HI (formed by the action of HCl on NH_4I) readily reduces arsenic acid, H_3AsO_4, to arsenious acid, H_3AsO_3, which reacts very rapidly with H_2S, while the H_3AsO_4 reacts very

[1] $AsCl_3$ solution is prepared by dissolving As_2O_3 in excess of HCl, and therefore contains free HCl.

[2] This precipitate contains As_2S_5 and $As_2S_3 + S$ in varying proportions, according to the conditions.

slowly. The HI is continuously regenerated by the H_2S from the I_2 formed in the reduction of the H_3AsO_4. The reactions involved are:

(1) $2H_3AsO_4 + 4HI \rightarrow 2H_3AsO_3 + 2H_2O + 2I_2$
(2) $2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$
(3) $2I_2 + 2H_2S \rightarrow 4HI + 2S.$

Adding and canceling substances occurring on both sides, the total equation is:

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_3 + 2S + 8H_2O.$$

3. *Formation and Decomposition of Ammonium Thioarsenate.*—Add $(NH_4)_2S_x$[1] to a little As_2S_3 from (**24**, 2), warming gently (E). The final solution contains $(NH_4)_3AsS_4$. Reserve for later use. (Separation from Cu Subgroup.)

What is the formula for ammonium arsenate? This brings out the chemical similarity of what two elements? (See Periodic Table.)

Acidify a little of the yellow solution containing $(NH_4)_3AsS_4$ with a little dilute HCl (E). The precipitate contains arsenic as As_2S_5. Reserve for (**24**, 4), below.

In order to be able to distinguish between the colors of arsenic sulfide and precipitated sulfur, acidify a little $(NH_4)_2S_x$ in a test tube with dilute HCl (E). What are the colors in question?

4. *Insolubility of Arsenic Pentasulfide in Hydrochloric Acid.*—Add to a little As_2S_5 from (**24**, 3) concentrated HCl, and heat nearly to boiling. Is there any apparent effect? (Separation of As_2S_5 from Sb_2S_3).

5. *Precipitation of Magnesium Ammonium Arsenate.*—To 2 cc. of water add 1 or 2 drops of K_3AsO_4 solution. Add about 1 cc. of "magnesia mixture"[2] (*i.e.*, $Mg(NO_3)_2 + NH_4NO_3$), and filter into the mixture concentrated NH_4OH (side shelf) to make the mixture strongly alkaline (about 1 cc.). Shake vigorously. The precipitate is $MgNH_4AsO_4$ (E). (Separation of As from Sb.) Reserve for (**24**, 6).

Notes.—1. The purpose of the NH_4NO_3 is to prevent the formation of a precipitate of $Mg(OH)_2$ by the NH_4OH. The NH_4OH is feebly ionized according to the equation, $NH_4OH \rightleftarrows NH_4^+ + OH^-$. The high concentration of the NH_4^+ ions from the highly ionized NH_4NO_3 displaces the equilibrium

[1] In writing equations, consider $(NH_4)_2S_x$ as containing $(NH_4)_2S$ and S.

[2] The usual form of magnesia mixture contains $MgCl_2$ (or $MgSO_4$) + NH_4Cl. The nitrates are used here, since the chlorides interfere with the subsequent formation of the Ag_3AsO_4 precipitate.

backward to such an extent that there are not enough OH^- ions left in the solution to form even enough $Mg(OH)_2$ to saturate the solution.

2. $MgNH_4AsO_4$ precipitates best from concentrated solutions. This explains the use of small volumes of the various reagents.

6. *Formation of Silver Arsenate.*—Filter the mixture containing the $MgNH_4AsO_4$ precipitate formed in the preceding experiment, and wash with a few cubic centimeters of NH_4OH which have been diluted with 4 or 5 volumes of water. Pour over the residue on the filter paper a few cubic centimeters of $AgNO_3$ solution which have been acidified with a few drops of $HC_2H_3O_2$. The chocolate precipitate is Ag_3AsO_4 (E).

Notes.—1. The $MgNH_4AsO_4$ is washed with NH_4OH solution instead of water to prevent its hydrolysis into $MgHAsO_4$, which is much more soluble than $MgNH_4AsO_4$, and might therefore be lost. The equation for this hydrolysis is: $MgNH_4AsO_4 + H_2O \rightleftarrows MgHAsO_4 + NH_4OH$.

2. $AgNO_3$ converts $MgNH_4AsO_4$ into Ag_3AsO_4, since the latter is much less soluble, and gives a much smaller concentration of AsO_4^{---} ions.

3. The purpose of the $HC_2H_3O_2$ is to neutralize the NH_4OH on the paper, since the latter dissolves Ag_3AsO_4. It also prevents the formation by the NH_4OH of any brown Ag_2O.

(25) Antimony, Sb^{+++}. 1. *Hydrolysis of Antimony Trichloride.* To 2 or 3 cc. of antimony trichloride solution, $SbCl_3$, add 10 cc. of water (?). Now add concentrated HCl drop by drop (?). Write a single reversible equation to represent both reactions (E).

2. *Solubility of Antimony Hydroxide in Tartrates.*—To 1 or 2 cc. of $SbCl_3$ solution add excess of NH_4OH (E), and then potassium hydrogen tartrate ("cream of tartar") solution, $KHC_4H_4O_6$ (R, E).

Note.—Antimony compounds, provided they are not too insoluble (*e.g.*, Sb_2S_3), dissolve in tartrate solutions, forming stable antimony-tartrate ions, as $SbOC_4H_4O_6^-$.

3. *Properties of Antimony Sulfide.*—Dilute 1 or 2 cc. of $SbCl_3$ solution to about 50 cc. in an Erlenmeyer flask (pay no attention to any precipitation of SbOCl) and saturate the mixture with H_2S (E). Note the color of the precipitate (?). Warm, and wash by decantation. Warm the residue with some freshly prepared $(NH_4)_2S$ solution (prepared by saturating NH_4OH with H_2S) (E). What is the name of the product? Write the equation for acidifying a solution containing $(NH_4)_3SbS_3$ with HCl (E).

What would be formed if Sb_2S_3 were dissolved in yellow ammonium sulfide solution, $(NH_4)_2S_x$ (E)? Write the equation for the action of HCl on the product (E).

Exercises

1. $Bi(NO_3)_3$ solution may give a precipitate of BiOCl with dilute HCl. Why, then, is Bi^{+++} not in Group I? Recall definition of Group I.
2. What are the names of the subgroups of Group II? What is the basis of this grouping?
3. Identify the following members of Group II:
   (*a*) What ion forms an insoluble sulfate?
   (*b*) What ions form brown sulfides? Yellow sulfides?
   (*c*) What ion forms a yellow chromate insoluble in $HC_2H_3O_2$?
   (*d*) What ion forms a yellow sulfide soluble in $(NH_4)_2S_x$, insoluble in saturated $H_2C_2O_4$?
   (*e*) What ions form NH_3 complexes similar to that of Ag^+?
   (*f*) What ion of the Tin Subgroup forms a sulfide insoluble in colorless $(NH_4)_2S$?
4. What step might be omitted in a Group II analysis if Pb^{++} were known to be absent?
5. What is the gas evolved when a sulfide dissolves in dilute HNO_3? Explain why it cannot be H_2S.
6. Calculate the concentration of the acid if 4 cc. of dilute HCl (6N, specific gravity = 1.12) is diluted to a volume of 100 cc.
7. Give a theory for the reactivity of the nascent state.
8. How is the valence of an element affected by (*a*) oxidation, (*b*) reduction?
9. Could $PbSO_4$ be converted into $Pb(NO_3)_2$ by evaporating it with an excess of concentrated HNO_3?
10. Refer to the "Electromotive Series" in the Appendix (page 126) and explain why Fe is the most suitable metal for separating Cu^{++} from Cd^{++}. What would happen if Zn were used?
11. What is the color of the sulfur precipitated from $(NH_4)_2S_x$ upon acidification with an acid (*a*) before boiling? (*b*) After continued boiling?
12. What substance is used to catalyze the precipitation of arsenic sulfide from arsenate solutions by means of H_2S?
13. What is the meaning of the prefix "thio?"
14. What is the effect of the presence of ammonium salts on the ionization of NH_4OH?
15. What sort of agent is the excess sulfur in $(NH_4)_2S_x$? Illustrate by its reaction with As_2S_3 or SnS.
16. What are the two stages in the reduction of Sn^{++++} by Al? The use of a large amount of Al would give what product? Is it the one required in the test?
17. AgCl is less soluble than Ag_3AsO_4. What would happen if a precipitate of Ag_3AsO_4 were washed with a solution containing NH_4Cl? Would Ag_3AsO_4 ever form in the presence of excess of chlorides?
18. Why will tartrates dissolve $Sb(OH)_3$ and not Sb_2S_3?

19. Indicate reagents and products in the following one-step separations:

(*a*) $\left\{ \begin{matrix} Bi(NO_3)_3 \\ Cd(NO_3)_2 \end{matrix} \right\}$ (reagent) → (products)

(*b*) $\left\{ \begin{matrix} HgS \\ As_2S_5 \end{matrix} \right\}$ ..... → .....

(*c*) $\left\{ \begin{matrix} Pb(NO_3)_2 \\ Cu(NO_3)_2 \end{matrix} \right\}$ ..... → .....

(*d*) $\left\{ \begin{matrix} As_2S_5 \\ SnS_2 \end{matrix} \right\}$ ..... → .....

(*e*) $\left\{ \begin{matrix} HgS \\ CdS \end{matrix} \right\}$ ..... → .....

20. An unknown solution containing only Group II ions gives with H_2S a brown precipitate, partially soluble in $(NH_4)_2S_x$. The brown residue dissolves in dilute HNO_3 to a colorless solution which gives no precipitate with H_2SO_4, but a white one with NH_4OH. The yellow $(NH_4)_2S_x$ filtrate gives upon acidification a yellow precipitate, soluble in concentrated $H_2C_2O_4$ solution. What ions are indicated?

ANALYSIS

The solution may be the filtrate from (**14**), or it may be an unknown on Group II only. Group II unknowns sometimes contain precipitates, such as $PbCl_2$, BiOCl, SbOCl, or $SnO_2.xH_2O$. In such a case filter and wash the precipitate, first with 4 cc. of hot dilute HCl, and then with 10 cc. of hot water, adding both filtrates to the main solution. Test the residue[1] for metastannic acid, $SnO_2.xH_2O$, by adding 10 cc. of dilute HCl and a piece of Al wire, and proceeding according to (**35**).

(**26**) **Regulation of Acidity.**—If the free acidity of the solution is known to be 4 cc. of dilute HCl (or its equivalent) in a volume of 40 cc., no further regulation is necessary. Proceed at once to (**27**).

If the amount of free acid is unknown,[2] place the solution in a small Pyrex beaker or casserole,[3] add 5 cc. of concentrated HNO_3,

[1] The residue might also contain $PbSO_4$, but it is presumed that this insoluble salt is absent from unknowns issued to students at this stage of the course.

[2] In solutions containing Group II only, this regulation of acidity is unnecessary, since the completeness of the precipitation may be determined in the usual way, *viz.*: by diluting the filtrate with a volume of water and resaturating with H_2S.

[3] The use of a casserole is to be preferred, since by holding it in the hand and shaking constantly the evaporation can be carried out over an open flame much more rapidly and without risk of excessive heating.

and evaporate to a paste. Take care not to ignite (see page vii) the residue, since in that case Hg might be lost by volatilization and Sn might be converted into an oxide insoluble in HCl. Moisten the residue with a little concentrated HCl, and again evaporate almost to dryness. Now add 4 cc. of dilute HCl and an equal volume of water, and warm (do not boil) until solution is complete. Cautious stirring with a stirring rod or a small porcelain spatula may aid in bringing the substance into solution.

Notes.—1. General unknowns may contain free acid in considerable excess over the proper value (4 cc. of dilute HCl), and this excess must be removed in order to precipitate the more soluble sulfides like CdS and PbS, which are more or less soluble in acid solutions of greater concentration. The presence of acetates also interferes by reducing the effective concentration of the acid so that the more insoluble sulfides of Group III (ZnS, for example) may be precipitated along with those of Group II.

2. By means of the evaporation with concentrated HNO_3, all free acids (except non-volatile acids like H_2SO_4 and H_3PO_3) are removed by vaporization; $HgCl_2$ and $AsCl_3$, which are volatile in steam, are converted into non-volatile $Hg(NO_3)_2$ and H_3AsO_4; acetates are wholly expelled; and any organic matter, which might interfere with the precipitation of $Al(OH)_3$ and $Cr(OH)_3$ in Group III, is destroyed.

(**27**) **Precipitation.**—Dilute the solution to 40 cc., heat nearly to boiling in an H_2S precipitation flask, add 1 cc. of NH_4I solution, and saturate the hot solution with H_2S. The precipitation may proceed slowly, and for this reason the H_2S should be passed into the solution for not less than 5 minutes. Note carefully the color changes during the precipitation, and try to interpret them. Cool the mixture, add 60 cc. of cold water, and, without filtering, saturate the cold solution with H_2S, shaking occasionally. Allow the mixture to stand for 10 minutes. Filter, and wash the precipitate thoroughly with small amounts of hot water, adding the first washings to the main filtrate and rejecting the rest. Reserve the filtrate[1] for (**50**); and analyze the precipitate[2] according to (**28**) and subsequent procedures.

[1] If the unknown contains Group II only, so that the acid concentration was not adjusted by (**26**), this filtrate should be diluted with a large volume of water and saturated again with H_2S in order to insure complete precipitation.

[2] A white precipitate indicates the absence of Group II sulfides. It is usually finely divided sulfur, produced by the oxidation of the H_2S by oxidizing agents present in the solution. The most important of these are: ferric

Notes.—1. Many of the precipitated sulfides are colloidal substances, which clog up the pores of the filter paper; consequently the filtration proceeds very slowly. Heat and the presence of strong electrolytes (NH_4NO_3 and NH_4Cl are usually used) make them more readily filterable. As far as possible, colloidal precipitates should be washed by decantation.

2. The sulfides do not precipitate simultaneously, but more or less in the order of their solubility, *viz.:* As_2S_3, HgS, CuS, Sb_2S_3, Bi_2S_3, SnS_2, PbS, SnS, and CdS. That is to say, little or none of any of these substances is precipitated until the precipitation of all of the sulfides preceding it in the list is complete. As_2S_5, on account of its low speed of formation, may be the last to form, notwithstanding the fact that it is the most insoluble sulfide of the group.

3. By careful observation of the colors shown by the precipitate as it forms, much valuable information may be obtained with regard to its composition. The student should review his notes on the preliminary experiments on Group II in this connection.

(28) Separation of the Copper and Tin Subgroups.—Place the precipitate[1] in a large test tube, add 10 cc. of $(NH_4)_2S_x$ solution, and warm just below the boiling point[2] for 10 minutes. Shake or stir frequently, so as to break down large masses of the precipitate and give the $(NH_4)_2S_x$ access to all parts of the solid. Dilute with an equal volume of water and filter.

To ascertain whether the Tin Subgroup has been completely removed, repeat the extraction with 5 cc. more of the $(NH_4)_2S_x$, dilute the filtrate to 10 cc., and acidify *a small portion* with dilute HCl. If the precipitate is finely divided and white, the separation is sufficiently complete; on the other hand, if the

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salts (yellow-brown), which are reduced to ferrous salts (faint green); dichromates (orange), reduced to chromic salts (green); permanganates (purple), reduced to manganous salts (colorless); chlorates and peroxides, which show no color changes upon reduction. These color changes should be carefully noted, since they indicate the presence of certain substances in the solution.

Sometimes a little $BaSO_4$ is precipitated at this point. Very active oxidizing agents, like permanganic acid, $HMnO_4$, may oxidize H_2S to H_2SO_4, the latter precipitating Ba^{++} as $BaSO_4$. In an elementary course, no account need be taken of the presence of this substance in the precipitate.

[1] If the amount of the precipitate is small, remove the paper from the funnel, tear off and reject that portion of the paper containing none of the precipitate, and digest paper and precipitate in 3 or 4 cc. of $(NH_4)_2S_x$.

[2] A convenient way for carrying out this operation is to place the test tube in a beaker of water, and heat the latter until the mixture in the tube just shows signs of boiling.

precipitate shows a yellow or orange tint, continue the extraction, using 5-cc. portions of $(NH_4)_2S_x$, until a portion of the fresh filtrate gives no colored precipitate upon acidification with dilute HCl.

Reserve the residue for (**29**). Combine all the unacidified filtrates known to contain the Tin Subgroup, and treat by (**34**) or by (**38**). (See footnote, page 30.)

TABLE III.—PRECIPITATION OF GROUP II AND SEPARATION OF THE COPPER AND TIN SUBGROUP

(**27**) Solution: Ions of Group II and subsequent groups in a volume of 40 cc. containing 4 cc. of dilute HCl. Heat, add 1 cc. of NH_4I solution and saturate with H_2S. Cool, add 60 cc. of water, and saturate again with H_2S. Filter, and wash precipitate.

(**28**) Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, SnS, SnS_2, As_2S_3, As_2S_5, Sb_2S_3. Wash and digest in warm $(NH_4)_2S_x$. Filter, wash precipitate.	Filtrate: Groups III, IV, V. (See Table VII)
Residue: HgS, PbS, Bi_2S_3, CuS, CdS. (See Table IV)	Filtrate: $(NH_4)_2SnS_3$, $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2S_x$. (See Tables V or VI)

(**29**) **Mercury.**—Wash the residue from (**28**) thoroughly with hot water,[1] and transfer it to a beaker or casserole. If the amount of the precipitate is too small to admit of this, tear off the part of the paper containing the residue, and use it instead. Add 10 to 20 cc. (depending on the amount of the precipitate) of a mixture of 1 volume of dilute HNO_3 with 2 volumes of water, cover with a watch glass and boil gently for 2 or 3 minutes. Filter, wash with a little water, and reserve the filtrate for (**30**).

A yellowish or gray residue, tending to float in hot HNO_3 solution, is impure sulfur, and may be discarded. If the residue is dark, Hg^{++} may be present. Place it, along with a portion of the paper, if the amount is very small, in a small beaker or casserole, and boil with a few cubic centimeters of aqua regia

[1] If the precipitate tends to run through the filter paper, add some solid NH_4NO_3 to the wash water. (See (**27**, note 1).)

(3 volumes of concentrated HCl and 1 volume of concentrated HNO_3) until the excess of the HNO_3 has been decomposed; that is, as long as brown fumes of NO_2 appear. Dilute to about 15 cc., filter and add $SnCl_2$ solution to the filtrate. A gray or black precipitate indicates the presence of Hg^{++}.

(**30**) **Lead.**—To the filtrate from (**29**) add 3 or 4 cc. of concentrated H_2SO_4 and evaporate in a Pyrex beaker until dense white fumes of SO_3 begin to come off. Let the mixture stand until it is thoroughly cooled, and then slowly pour it into 15 or 20 cc. of water in another beaker, and rinse out the first beaker with some of the diluted solution. Stir well, cool again, and let the mixture stand for a few minutes. Filter, and wash the precipitate, first with dilute H_2SO_4 to which its own volume of water has been added, and then with a little water. Combine the first washings with the main filtrate, and reserve for (**31**).

A white precipitate is usually $PbSO_4$, though sometimes $(BiO)_2SO_4$ appears at this point, if the washing with H_2SO_4 was not thorough. Pour over the residue several times a 10-cc. portion of hot $NH_4C_2H_3O_2$ solution, reheating before each extraction. To the filtrate add 2 or 3 drops of $K_2Cr_2O_7$ solution. A yellow precipitate, $PbCrO_4$, insoluble in $HC_2H_3O_2$, indicates the presence of Pb^{++}.

Notes.—1. $PbSO_4$ is somewhat soluble in concentrated H_2SO_4, which appears to convert it into a soluble acid salt, $Pb(HSO_4)_2$. Upon dilution, this salt is decomposed, forming the decidedly insoluble $PbSO_4$ again. The equation may be written reversibly, thus: $PbSO_4 + H_2SO_4 \rightleftarrows Pb(HSO_4)_2$.

2. Lead and bismuth salts in neutral solution both give, with $K_2Cr_2O_7$ solution, yellow precipitates, $PbCrO_4$ and $(BiO)_2Cr_2O_7$, respectively. These substances differ in that $(BiO)_2Cr_2O_7$ is readily soluble in $HC_2H_3O_2$, while $PbCrO_4$ is not.

(**31**) **Bismuth.**—To the filtrate from (**30**) add NH_4OH until, after the mixture has been shaken, a drop of it on a stirring rod turns red litmus paper blue, and then add 1 or 2 cc. in excess. A white, gelatinous precipitate is probably $Bi(OH)_3$. Shake, filter, and wash once with a little cold water. Reserve the filtrate for (**32**). Prepare some fresh Na_2SnO_2 solution according to the directions in the footnote to (**20**, 5), page 15, and pour over the residue. A black precipitate is metallic Bi.

Note.—The purpose of the excess NH_4OH is to redissolve any $Cu(OH)_2$ or $Cd(OH)_2$ that might precipitate at this point.

(**32**) **Copper.**—A blue color in the filtrate from (**31**) is a sufficient test for Cu^{++}. In such a case proceed at once to (**33**). If the solution is practically colorless, only a trace of Cu^{++} can be present. In that case, take a small portion of the solution (reserving the larger portion for (**33**)), acidify it with dilute H_2SO_4 (litmus test), and add 1 or 2 drops (not more) of $K_4Fe(CN)_6$ solution. A red coloration, due to $Cu_2Fe(CN)_6$, indicates Cu^{++}.

Note.—Excess of $K_4Fe(CN)_6$ may interfere with the test for Cu^{++} by precipitating white-yellow $Cd_2Fe(CN)_6$, which may largely cover up the red color of $Cu_2Fe(CN)_6$

(**33**) **Cadmium.**—If Cu^{++} is absent, to the remainder of the solution from (**32**) add dilute H_2SO_4 to faint acidity (litmus test) and saturate with H_2S. A yellow precipitate, CdS, indicates Cd^{++}.

If Cu^{++} is present, transfer the solution to a beaker, add dilute H_2SO_4 until the deep-blue color due to $Cu(NH_3)_4^{++}$ is bleached out, and then 3 or 4 cc. in excess. Add about 1 cc. of Fe filings, cover with a watch glass, and boil gently for several minutes. Filter into an H_2S precipitation flask, and, if the solution is not still acid, add a few cubic centimeters more of dilute H_2SO_4. Saturate with H_2S. A yellow precipitate is CdS.

Sometimes, owing to faulty technique, a black precipitate is obtained. Filter, wash, and boil the residue with 3 cc. of dilute H_2SO_4 and 10 cc. of water. Filter, dilute the filtrate with several volumes of water, and saturate with H_2S. A yellow precipitate indicates the presence of Cd^{++}.

Note.—The black precipitate obtained upon saturating the filtrate from the Fe filings with H_2S may contain, besides CdS, such substances as HgS, CuS, PbS, and FeS. The H_2SO_4 treatment does not dissolve either HgS or CuS, and converts PbS into insoluble $PbSO_4$. The CdS and FeS dissolve, and only the CdS is again precipitated from the diluted solution.

*The best method[1] for testing for Cd^{++} in the presence of Cu^{++} involves the use of NaCN or KCN solution, and, on account

[1] Experiments and procedures marked with an asterisk (*) may be omitted at the discretion of the instructor. They are always alternative procedures, as in this case, or else tests or methods required in special or advanced analyses only. The student should consult with his instructor in all such cases.

of the exceedingly poisonous nature of these materials, is not suitable for elementary students. The procedure is as follows:

To the blue solution from (**32**) add NaCN or KCN solution until the blue color is bleached out, and then saturate with H_2S. A yellow precipitate is CdS. A black precipitate, due to the incomplete removal of Hg^{++} and Pb^{++}, should be washed free from cyanides and then boiled gently for several minutes in a covered beaker with 5 cc. of dilute H_2SO_4 and 20 cc. of water. Filter, dilute to 100 cc., and saturate with H_2S. Yellow CdS will be precipitated if Cd^{++} is present. (See note above, this section.)

TABLE IV.—ANALYSIS OF THE COPPER SUBGROUP

(**29**) Residue from the $(NH_4)_2S_x$ extraction: HgS, PbS, Bi_2S_3, CuS, CdS. Boil with dilute HNO_3 (dilute HNO_3 + 2 volumes of water). Filter, wash precipitate.

Residue: HgS, S. Dissolve in aqua regia, boil out excess acid, and filter out any S. Dilute, add $SnCl_2$. Gray precipitate: Hg_2Cl_2-Hg. white black	(**30**) Filtrate: Pb^{++}, Bi^{+++}, Cu^{++}, and Cd^{++} as nitrates. Add H_2SO_4, evaporate to SO_3 fumes. Dilute, filter.			
	Precipitate: $PbSO_4$. Dissolve in $NH_4C_2H_3O_2$. Add $K_2Cr_2O_7$, $HC_2H_3O_2$. Precipitate: Yellow $PbCrO_4$.	(**31**) Filtrate: Bi^{+++}, Cu^{++} and Cd^{++} as sulfates. Add NH_4OH, filter.		
		Precipitate: $Bi(OH)_3$. Add Na_2SnO_2. Residue: Black Bi.	(**32**) Filtrate: $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$ as sulfates. If blue, proceed to (**33**); if indecisive, divide, acidify smaller portion with H_2SO_4, add $K_4Fe(CN)_6$. Brown precipitate (or rose color): $Cu_2Fe(CN)_6$. If Cu^{++} is found, treat remaining solution by (**33**); if Cu^{++} is absent, proceed directly to (A).	
			(**33**) Add H_2SO_4, Fe filings, boil, and filter.	
			Prec.: Cu-Fe. Reject.	Filtrate: Cd^{++} and Fe^{++} as sulfates. Treat by (A).
			(A) Acidify with H_2SO_4, saturate with H_2S. Precipitate: Yellow CdS.	

THE TIN SUBGROUP[1]

Method A

(**34**). Strongly acidify the filtrate from (**28**) in a beaker with dilute HCl, and boil to expel the H_2S. To the hot mixture, add, with stirring, solid potassium chlorate, $KClO_3$, *in small amounts*, until the precipitate is reduced to a residue which *floats* on the surface of the liquid. If necessary, add a few drops of concentrated HCl to hasten the reaction. Boil for 5 minutes to expel excess of acid, dilute to 75 cc., and add 25 cc. of saturated oxalic acid solution. Heat to boiling, add 1 cc. of NH_4I solution, and saturate the hot solution for 10 minutes with H_2S. A yellow-to-orange precipitate indicates the presence of As or Sb, or both. Reheat the filtrate, and saturate it again with H_2S to insure complete precipitation of As and Sb. If a second precipitate forms, add it to the first, and reserve the combined precipitate for (**36**). Treat the filtrate by (**35**).

Notes.—1. A white precipitate obtained upon acidifying the filtrate from (**28**) is sulfur, and indicates either the absence of the Tin Subgroup ions or their presence in small quantities only.

2. The $KClO_3$ treatment oxidizes the sulfides to the corresponding acids; *e.g.*, $3As_2S_5 + 5KClO_3 + 9H_2O \rightarrow 6H_3AsO_4 + 5KCl + 15S$.

(**35**) **Tin.**—Evaporate the filtrate from (**34**) in an open beaker or dish to a volume not greater than 50 cc. Introduce a single piece of aluminum wire[2] (side shelf), and heat nearly to boiling. Introduce, in small amounts, dilute HCl until a mild effervescence begins. When the Al is completely dissolved, boil 2 or 3 minutes to redissolve any metallic tin that may have separated. If large amounts of tin are present, it may be necessary to add concentrated HCl to effect solution. Filter at once into 5 cc. of $HgCl_2$ solution in a test tube. If a red precipitate of mercuric iodide forms, redissolve it in a small amount of dilute HCl. A white precipitate of Hg_2Cl_2 or a gray-black precipitate of Hg, *appearing immediately*, indicates the presence of a Sn ion in the original solution.

[1] Before beginning the analysis of the Tin Subgroup, the student should consult his instructor as to whether Method A or Method B should be used.

[2] These pieces of Al wire are cut so as to weigh about 0.05 gram.

Notes.—1. Commercial Al contains small amounts of carbon, which may appear as a slight gray-black insoluble residue. It also contains small amounts of iron, which may separate during the action, but redissolve just as soon as the Al is used up.

2. Upon standing, $SnCl_2$ solution is oxidized by the air to $SnCl_4$, which gives no reaction with $HgCl_2$ solution.

3. Sometimes, owing to incomplete precipitation by H_2S in (**34**), the treatment with Al causes the separation of a black precipitate of metallic antimony and arsenic. Such a precipitate should be filtered out and combined with the sulfide precipitate obtained in (**34**) and reserved for (**36**).

(**36**) **Arsenic.**—Wash the residue from (**34**) and transfer it (along with the filter paper, if necessary) to an Erlenmeyer flask. Add about 20 cc. of NH_4OH and about 10 cc. of H_2O_2 solution. Warm gently, with frequent shaking, until solution is complete or only a milky-white residue (sulfur) remains. More H_2O_2 may be added, if necessary. Filter, wash, and reject the precipitate. Evaporate the filtrate in a small beaker to about 20 cc., and filter into it about 2 cc. of Rochelle salt solution, $KNaC_4H_4O_6$, 3 or 4 cc. of concentrated NH_4OH (side shelf), and 3 or 4 cc. of "magnesia mixture."[1] Stir well, and allow the mixture to stand for at least 30 minutes. A precipitate of basic magnesium tartrate, $MgC_4H_4O_6.Mg(OH)_2$, may form along with any $MgNH_4AsO_4$. At the end of 30 minutes filter, reserving the filtrate for (**37**).

Wash the precipitate with a very little dilute NH_4OH (desk reagent + 3 volumes of water). Then pour over the residue in the funnel a mixture of 1 cc. of $AgNO_3$ solution, a few drops of $HC_2H_3O_2$, and 2 or 3 volumes of water. A brown color (due to Ag_3AsO_4) shows the presence of AsO_4^{---}.

Notes.—1 The NH_4OH–H_2O_2 treatment converts As_2S_5 and Sb_2S_5 into $(NH_4)_3AsO_4$, $(NH_4)_3SbO_4$, and $(NH_4)_2SO_4$.

2. The $KNaC_4H_4O_6$ prevents the precipitation of H_3SbO_4 by converting it into complex molecules, as $KSbO_2C_4H_4O_6$ and $NaSbO_2C_4H_4O_6$.

3. The $MgNH_4AsO_4$ precipitate tends to form slowly, and for this reason the mixture is allowed to stand for 30 minutes, so as to make possible a complete separation of the As.

[1] See footnote, page 20.

(37) Antimony.—Saturate the filtrate from **(36)** with H_2S. If a precipitate forms, filter, and discard the residue. Acidify (litmus test) the filtrate with HCl, and heat to boiling. A yellow precipitate, changing to red upon heating the mixture, indicates the presence of Sb.

If the precipitate, after boiling, is yellow and not orange, it is probably As_2S_5 which was not completely removed in **(36)**. In such a case, treat it again by **(36)**, and test the filtrate again for Sb.

TABLE V.—ANALYSIS OF THE TIN SUBGROUP
(Method A)

(34) Solution: $(NH_4)_2SnS_3$, $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, excess $(NH_4)_2S_x$. Acidify with dilute HCl, boil, add solid $KClO_3$ until sulfides are decomposed. Dilute to 75 cc., add 25 cc. of sat. $H_2C_2O_4$, and heat to boiling. Add NH_4I, and saturate with H_2S. Filter, reheat filtrate, and saturate again with H_2S. Filter, wash precipitate.

(35) Filtrate: $Sn(C_2O_4)_2$. Concentrate to 50 cc., add Al wire and HCl. Boil to dissolve Sn, filter into $HgCl_2$ solution.

Precipitate: White Hg_2Cl_2 or gray Hg.

(36) Precipitate: As_2S_5, Sb_2S_3, S. Add NH_4OH and H_2O_2 and warm to complete reaction. Evaporate to 20 cc., add 2 cc. $KNaC_4H_4O_6$, 3 or 4 cc. conc. NH_4OH, and 3 or 4 cc. "magnesia mixture." Allow to stand 30 minutes, filter, wash precipitate with dilute NH_4OH.

Precipitate: White $MgNH_4AsO_4$ (+ $MgC_4H_4O_6$.-$Mg(OH)_2$.) Pour dilute $AgNO_3$ + $HC_2H_3O_2$ over filter paper.

Residue: Brown Ag_3AsO_4.

(37) Filtrate: $(NH_4)_3SbO_4$ in tartrate solution. Saturate with H_2S, filter off any precipitate. Acidify filtrate with HCl, heat to boiling.

Precipitate: Orange Sb_2S_3.

Method B[1]

(38) Precipitation of the Tin Subgroup.—Combine all the filtrates from **(28)** known to contain the Tin Subgroup, and acidify with dilute HCl (litmus test). Avoid an unnecessary excess of the acid. Boil gently for a few minutes to expel H_2S.

[1] This is a modification of the scheme given by A. A. Noyes in his "Qualitative Chemical Analysis of Inorganic Substances," 6th ed.

and to coagulate the precipitate. Filter promptly, wash with a little hot water, and reject the filtrate. A yellow-to-orange precipitate indicates the presence of the Tin Subgroup; a white precipitate is due to sulfur, and the Tin Subgroup sulfides are absent, or present in small quantity only. Sometimes the precipitate shows a brown or buff color, due to the presence of small amounts of HgS or CuS, which are slightly soluble in $(NH_4)_2S_x$; the Tin Subgroup may or may not be present.

(**39**) **Arsenic.**—Transfer the precipitate to a large test tube, add exactly 10 cc. of concentrated HCl, and place the tube in a beaker of hot water. Do not allow the contents of the tube to boil. If the mixture shows signs of boiling, remove the tube from the beaker for a moment. Digest just below the boiling point for not less than 10 minutes, and shake or stir frequently, so as to break down the larger masses of the precipitate. Dilute with 10 cc. of water, filter, and wash. Receive the filtrate in a graduated cylinder, and dilute to exactly 50 cc. with distilled water. Reserve this solution for (**40**).

Add 10 cc. of dilute HNO_3 to the residue and warm as long as brown fumes are given off. Dilute with 3 or 4 cc. of water, filter out the residue (impure sulfur), receiving the filtrate in a small Pyrex beaker. Evaporate to 5 cc., and add 1 cc. of "magnesia mixture."[1] If the solution is not acid, acidify with a few drops of dilute NHO_3. Filter if not perfectly clear. Filter[2] into the solution concentrated NH_4OH (side shelf) until the solution is strongly alkaline, shake vigorously, and allow the solution to stand an hour before deciding that the test is negative. A white crystalline precipitate, $MgNH_4AsO_4$, indicates the presence of an As compound in the original solution.

If the precipitate is not distinctly crystalline, the presence of AsO_4^{---} should be confirmed as follows: Filter, wash the precipitate, first with a little dilute NH_4OH (1 volume of the reagent + 3 volumes of water), and then with a little water. Pour over the residue on the paper some very dilute $AgNO_3$ solution, to which have been added several drops of $HC_2H_3O_2$. A brown color (due to Ag_3AsO_4) shows the presence of AsO_4^{---}.

[1] See footnote, page 20.

[2] Strong alkaline reagents attack the glass of the bottles, and tend to become "dreggy."

Notes.—1. If Sb_2S_5 or SnS_2 is present, there will be a certain amount of effervescence during the digestion of the Tin Subgroup sulfides in the 10 cc. of concentrated HCl, owing to the liberation of the H_2S formed by their dissolving in the acid. This reaction occurs almost wholly during the first stages of the digestion.

2. As_2S_5 is soluble in *boiling* concentrated HCl to an appreciable extent, since the equilibrium in the following reaction is displaced by the removal of the gaseous product, H_2S: $As_2S_5 + 8H_2O \rightarrow 2H_3AsO_4 + 5H_2S$.

3. The HNO_3 treatment converts As_2S_5 into H_3AsO_4 and S.

(40) Antimony.—Heat the solution from (**39**) just to boiling in an Erlenmeyer flask, wrap a towel around the flask to prevent heat losses, and saturate the hot solution with H_2S for 5 minutes. If no precipitate forms, add 5 cc. of water, reheat, and again saturate with H_2S. An orange precipitate, Sb_2S_3, indicates the presence of Sb^{+++}. Filter while hot, reserving the filtrate for (**41**).

If the precipitate is not distinctly orange in color, dissolve it in concentrated HCl in a beaker, add several volumes of water and a piece of Al wire[1] (side shelf). If necessary, warm until a vigorous reaction begins. The separation of a black precipitate, insoluble in HCl, and insoluble in NaOCl solution, confirms the presence of Sb.

Note.—The above method for separating Sb^{+++} from Sn^{++++} depends upon the fact that Sb_2S_3 is much less soluble than SnS_2, and for that reason can be precipitated from hot HCl solution, in which the latter is soluble.

(41) Tin.—Evaporate the filtrate from (**40**) to about 30 cc., and add a single piece of Al wire (side shelf) to the hot solution. A mouse-colored deposit on the Al and floating in the solution is probably metallic Sn. After the Al is all dissolved, boil the mixture gently for several minutes to redissolve any Sn, and filter the solution at once into 5 cc. of $HgCl_2$ solution in a test tube. A white precipitate of Hg_2Cl_2 or a gray-black precipitate of Hg confirms the presence of SnS_2 in the brown precipitate above.

Note.—$SnCl_2$ solutions on standing are oxidized by the air to $SnCl_4$, thus: $2SnCl_2 + 4HCl + O_2 \rightarrow 2SnCl_4 + 2H_2O$. For this reason the $HgCl_2$ test must be made promptly.

[1] These pieces of Al wire are cut so as to weigh about 0.05 gram each.

TABLE VI.—ANALYSIS OF THE TIN SUBGROUP
(Method B)

(**38**) Solution: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$, excess $(NH_4)_2S_x$. Dilute, acidify with dilute HCl, boil, filter, and wash precipitate. Reject the filtrate. (**39**) Digest the precipitate 10 minutes in 10 cc. of hot concentrated HCl. Dilute, filter, and wash precipitate. Dilute filtrate to 50 cc.

Residue: As_2S_5, S.
Heat with dilute HNO_3, filter, and evaporate. Add magnesia mixture, concentrated NH_4OH.
Precipitate:
White $MgNH_4AsO_4$.
Pour dilute $AgNO_3$ + $HC_2H_3O_2$ over the filter paper.
Residue:
Brown Ag_3AsO_4.

(**40**) Filtrate: $SbCl_3$, $SnCl_4$ in 50 cc. of solution. Heat to boiling, saturate hot with H_2S for 5 minutes, filter, wash precipitate.

Precipitate:
Orange Sb_2S_3.
Dissolve in HCl, add Al.
Precipitate, insoluble in HCl, NaOCl:
Black Sb.

(**41**) Filtrate: $SnCl_4$. Evaporate, add Al, heat until action is complete. Filter into $HgCl_2$ solution.
White precipitate, Hg_2Cl_2, or gray-black precipitate, Hg, indicates presence of Sn.

GROUP III. THE AMMONIUM SULFIDE GROUP

This group contains the cations of those metals whose sulfides (or hydroxides) are not precipitated by H_2S in dilute acid solution (*i.e.*, 0.25N HCl), but are precipitated by H_2S in NH_4OH solution containing ammonium salts. This combination of NH_4OH and H_2S is equivalent to $(NH_4)_2S$, so $(NH_4)_2S$ may be regarded as the group reagent.

Al^{+++} and Cr^{+++} are precipitated as $Al(OH)_3$ and $Cr(OH)_3$, their sulfides being completely hydrolyzed by water.

The presence of ammonium salts prevents the precipitation of hydroxides like $Mg(OH)_2$ and $Ca(OH)_2$, and of sulfides like CaS. The ammonium salts also diminish the solubility of $Al(OH)_3$ in the excess NH_4OH.

In the presence of phosphates, oxalates, borates, fluorides, etc., Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} may also be precipitated with this group, owing to the insolubility of such salts as $Ba_3(PO_4)_2$, CaC_2O_4, etc., in alkaline solutions.

This group is divided into two subgroups: (1) The Aluminium Subgroup, consisting of Al^{+++}, Cr^{+++}, and Zn^{++}, whose hydrox-

ides are soluble in NaOH solution in the presence of sodium peroxide, Na_2O_2; (2) The Iron Subgroup, consisting of Mn^{++}, Fe^{+++}, Ni^{++}, and Co^{++}, whose hydroxides are insoluble in NaOH solution in the presence of Na_2O_2.

PRELIMINARY EXPERIMENTS

(42) Aluminium, Al^{+++}. 1. *Hydrolysis of Aluminium Sulfide and Aluminium Carbonate.*—Prepare some diluted aluminium sulfate solution, $Al_2(SO_4)_3$, by adding about 4 volumes of water to a little of the side shelf reagent. To a portion of this in a test tube add NH_4OH (E). (SEPARATION OF Al^{+++} FROM CrO_4^{--}, Zn^{++}.) Save for comparison with the subsequent experiments.

Prepare some colorless ammonium sulfide solution, $(NH_4)_2S$, by passing H_2S into 10 cc. of NH_4OH, and treat a second portion of the diluted $Al_2(SO_4)_3$ with this reagent.

To a third portion of the diluted $Al_2(SO_4)_3$ solution add Na_2CO_3 solution.

Compare the three precipitates (?). Explain their identity by appropriate equations (E's).

Note.—The failure of $(NH_4)_2S$ and Na_2CO_3 to precipitate Al_2S_3 and $Al_2(CO_3)_3$ from solutions containing Al^{+++} salts is due to hydrolysis; that is, the decomposition of these salts by water. The following rules for hydrolysis are useful:

1. Salts of strong bases and strong acids are not perceptibly hydrolyzed; *e.g.*, NaCl.

2. Salts of strong bases and weak acids, or of weak bases and strong acids, are partially hydrolyzed; *e.g.*, Na_3PO_4 (alkaline to litmus), $AlCl_3$ (acid to litmus).

3. Salts of weak bases and weak acids are (generally) completely hydrolyzed; *e.g.*, Al_2S_3.

A general exception to these rules is that salts of low water solubility may be very stable, notwithstanding that both the base and acid represented may be very weak. $FePO_4$ is an example. This behavior indicates that a certain degree of solubility in water must precede hydrolysis.

2. *Amphoteric Nature of Aluminium Hydroxide.*—Prepare some $Al(OH)_3$ by the action of NH_4OH on $Al_2(SO_4)_3$ solution. Filter. By means of a spatula place portions of this precipitate in two test tubes. To one add a dilute acid; *e.g.*, HNO_3 (E); to the second add NaOH solution (E). What is the rôle of the

$Al(OH)_3$ in each case? Save the remainder of the precipitate for (**42**, 3).

Notes.—1. On account of its amphoteric nature, $Al(OH)_3$ is somewhat soluble in excess of NH_4OH. By precipitating in the presence of ammonium salts, and by heating the mixture just to boiling (to expel most of the excess NH_4OH), this precipitation may be made complete.

2. The solution of $Al(OH)_3$ in NaOH solution seems to contain the metaluminate, $NaAlO_2$, instead of the orthoaluminate, Na_3AlO_3. (See advanced textbooks for discussion.)

3. *Distinction between Aluminium Hydroxide and Silicic Acid.*—Dilute 2 or 3 drops of sodium silicate solution, Na_2SiO_3, to 10 cc., add NH_4Cl solution, and warm. The precipitate is silicic acid, for which H_2SiO_3 may be used as a representative formula. Note that it is somewhat similar in appearance to $Al(OH)_3$. Evaporate a portion of the mixture containing the precipitate to dryness in a Pyrex beaker, allow to cool, add dilute HCl, and warm. Filter and add dilute NH_4OH to the filtrate (?).

Evaporate the $Al(OH)_3$ precipitate from (**42**, 2) just to dryness in a similar way, extract with warm dilute HCl, and add NH_4OH to the filtrate (?). Write equations for the reactions involved (E's).

State how $Al(OH)_3$ may be distinguished from H_2SiO_3 (?).

Notes.—1. Alkaline solutions (*e.g.*, NaOH) attack glass and porcelain and become contaminated with soluble silicates, as Na_2SiO_3. Upon adding NH_4OH, these solutions give a precipitate that might easily be mistaken for $Al(OH)_3$.

2. Silicic acid upon evaporation to dryness is converted into SiO_2 with the loss of water. The SiO_2 residue is insoluble in dilute HCl.

4. *Formation of Lakes with Dyes.*—To some very dilute $Al_2(SO_4)_3$ solution in a test tube add 1 or 2 drops of aurin tricarboxylic acid solution and a slight excess of NH_4OH and heat to boiling. Note that the dye is absorbed by the $Al(OH)_3$, leaving the solution practically colorless. The insoluble compounds made by certain dyes with $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, etc., are known as "lakes."

(**43**) **Chromium, Cr^{+++}; Chromate, CrO_4^{--}; Dichromate, $Cr_2O_7^{--}$.** 1. *Amphoteric Properties of Chromium Hydroxide.*—Dilute 2 or 3 cc. of chromium chloride solution, $CrCl_3$, to about

10 cc. and divide into two parts. To one add NH_4OH, at first drop by drop (E), then in excess (?).

To the second part add NaOH solution, at first drop by drop (E), then in excess (E). Boil (?, E). Save for (**43**, 2).

Note.—The solution of $Cr(OH)_3$ in NaOH solution is supposed to contain sodium metachromite, $NaCrO_2$. As found above, the hydroxide is reprecipitated upon boiling, and does not readily revert to the soluble form.

2. *Oxidation of Chromium Hydroxide to Chromates.*—Transfer the solution containing the $Cr(OH)_3$ precipitate from the above test to a small beaker, and add about 1 gram of solid sodium peroxide,[1] Na_2O_2 (storeroom), in small portions, with stirring (E). What is the color of the solution? Boil to decompose excess of Na_2O_2, and acidify the Na_2CrO_4 solution with dilute HNO_3 (E). Note the change in color (?).

3. *The Peroxide Test for Chromates and Dichromates.*—Add a single drop of potassium dichromate solution, $K_2Cr_2O_7$, to about 5 cc. of water, acidify with a drop or two of H_2SO_4 or HNO_3, and add 2 cc. of ether and 1 cc. of hydrogen peroxide solution, H_2O_2, and shake promptly (?). The blue color is a very characteristic test for CrO_4^{--} and $Cr_2O_7^{--}$, but is not a test for chromic salts (*i.e.*, Cr^{+++} ions).

4. *Reduction of Dichromates by Hydrogen Sulfide.*—Acidify 2 cc. of $K_2Cr_2O_7$ solution with an equal volume of dilute HCl, dilute to 15 or 20 cc., and saturate with H_2S. What is the milky precipitate? Write equation (E). Boil, filter, and add NH_4OH to the filtrate (E). Account for the change in color under the action of the H_2S (?).

5. *Hydrolysis of Chromic Salts.*—$Cr(OH)_3$ is a weak base like $Al(OH)_3$. Write equations for the action of $(NH_4)_2S$ and Na_2CO_3 solutions on $CrCl_3$ solution (E's).

(44) Zinc, Zn^{++}. 1. *Solubility of Zinc Hydroxide in Ammonium Hydroxide and in Sodium Hydroxide Solutions.*—Dilute 2 cc. of zinc nitrate solution, $Zn(NO_3)_2$, to 10 cc., and add NH_4OH,

[1] Sodium peroxide is issued to the students on watch glasses at the storeroom, and in very small quantities. It is an exceedingly active oxidizing agent, and, when brought in contact with paper, towels, or wood, spontaneous combustion may take place. For this reason, the student is required to throw any excess of the material into the sink (not the slop jar) and to flush it into the drain with plenty of water. *Never store it in the desk.*

at first drop by drop (E), then in excess (E). (SEPARATION OF Zn^{++} FROM Al^{+++}.)

Repeat, using NaOH solution instead of NH_4OH, noting similar effects (E's).

Does $Zn(OH)_2$ behave as an acid in both cases? What would be the probable action of water on ammonium zincate, $(NH_4)_2ZnO_2$?

Note.—The solubility of $Zn(OH)_2$ in excess NH_4OH is due to the formation of the complex ion, $Zn(NH_3)_4^{++}$, which gives too low a concentration of Zn^{++} ions for $Zn(OH)_2$ to be precipitated even by strong bases like NaOH. It does, however, afford a high enough concentration of Zn^{++} ions for the complete precipitation of ZnS. This depends on the fact that the concentration of the S^{--} ions may be large in alkaline solutions, since the H^+ ions are almost wholly absent.

2. *Solubility of Zinc Sulfide.*—To some diluted $Zn(NO_3)_2$ solution in an Erlenmeyer flask add colorless ammonium sulfide, $(NH_4)_2S$—*i.e.*, add NH_4OH to alkalinity and then saturate with H_2S (E). What is the color of ZnS? Shake and divide the mixture into three portions. To one add a few drops of dilute HCl (?). To another, $HC_2H_3O_2$ (?). To the third, add 5 cc. of sodium acetate solution, $NaC_2H_3O_2$, and a few drops of dilute HCl (?).

Note.—The precipitation of ZnS depends wholly upon the presence in the solution of sufficient numbers of Zn^{++} and S^{--} ions. If a precipitate fails to form, it is because one of these ions (S^{--}, usually) is present in exceedingly small amount. Other ions have no effect except as they increase or diminish the number of these ions. ZnS does not form in the presence of strong acids, like HCl, because the large number of H^+ ions from the strong acid drive back the ionization of the H_2S, thus: $2H^+ + S^{--} \rightleftarrows H_2S$. (The "common ion effect.") On the other hand, if the salt of a weak acid, like acetic acid, is present, the anions of this weak acid will combine with the H^+ ions of the strong acid, removing them with practical completeness. This permits of an increased ionization of the H_2S, with the result that the S^{--} ions become numerous enough to precipitate the Zn^{++} ions as ZnS.

3. *Formation of Zinc Ferrocyanide.*—To 4 or 5 cc. of $Zn(NO_3)_2$ solution add a little potassium ferrocyanide solution, $K_4Fe(CN)_6$ (E). Now add a few drops of potassium chromate solution, K_2CrO_4. Does the presence of the latter interfere with this test for the Zn^{++} ion?

(45) Manganese, Mn^{++}. 1. *Precipitation of Manganous Hydroxide.*—Dilute 2 cc. of manganous nitrate solution, $Mn(NO_3)_2$, to 10 cc., bring to a boil (to expel dissolved air), and add NH_4OH (?). Boil a few cubic centimeters of NH_4NO_3 solution, and add it to one-half of the mixture containing the $Mn(OH)_2$ precipitate (?). Express both reactions by a single reversible equation (E). Reserve remainder of the $Mn(OH)_2$ mixture for the next experiment.

2. *Oxidation of Manganous Hydroxide to Maganese Dioxide.*—Cool the remainder of the $Mn(OH)_2$ mixture from the preceding experiment, add about 5 cc. of water, and shake vigorously, so as to saturate with air (E). Try the solubility of the product in NH_4NO_3 solution (?).

3. *Solubility of Manganese Dioxide.*—Add about 5 cc. of concentrated HNO_3 to a pinch of MnO_2 in a test tube, and boil (?). (Separation of MnO_2 from Fe^{+++}, Ni^{++},Co^{++}.) Dilute with 2 or 3 volumes of water, shake, and divide the mixture into two parts. To the first slowly add H_2O_2 solution (E). (This is a most convenient way to remove stains of MnO_2 from beakers, etc.) Reserve the second portion for the next experiment.

4. *Oxidation of Manganese Dioxide to Permanganic Acid.*—To the MnO_2-HNO_3 mixture from the preceding experiment, add a little lead dioxide, PbO_2, and boil for a minute. Allow the mixture to settle and note the color of the supernatant liquid (?). Write the equation (E).

(46) Iron: Ferrous, Fe^{++}, and Ferric, Fe^{+++}.—1. *Reduction of Ferric Salts by Hydrogen Sulfide.*—Dilute 2 cc. of ferric chloride solution, $FeCl_3$, to 10 cc., add 5 cc. of dilute HCl, and saturate with H_2S. Boil for a few moments and filter. What is the color of the filtrate? What is the precipitate on the filter paper? Express all the results by a properly labeled equation (E).

2. *Oxidation of Ferrous Hydroxide.*—Dilute some ferrous sulfate solution, $FeSO_4$, in a small beaker, and add NaOH solution (E). Now add slowly, with stirring, Na_2O_2, until the color change is complete (E). Indicate the colors of the precipitates.

Note.—Ferrous hydroxide is really white; the green color is due to the presence of Fe^{+++} in the $FeSO_4$ solution.

3. *Insolubility of Ferric Hydroxide in Ammonium Hydroxide.*—To a little $FeCl_3$ solution add NH_4OH (E). Is the precipitate

soluble in excess NH_4OH? (SEPARATION OF Fe^{+++} FROM Ni^{++} AND Co^{++}.)

4. *Tests for Fe^{+++} and Fe^{++} Ions.*—To some very dilute $FeCl_3$ solution add a few drops of ammonium thiocyanate solution, NH_4SCN (E).

Test the $FeSO_4$ solution for Fe^{+++} by this reagent (?). What impurity is indicated?

Treat some dilute HNO_3 with dilute NH_4SCN solution (?). Heat the mixture to boiling (?). Is the red color with NH_4SCN solution an infallible test for Fe^{+++}?

Note.—The reaction of NH_4SCN with Fe^{+++} solutions depends on the formation of the slightly ionized $Fe(SCN)_3$ molecules. This test may be made in the presence of considerable amounts of HCl without appreciable loss in sensitiveness. This is due to the fact that HSCN is a highly ionized acid, and therefore the presence of the H^+ ions from the HCl reduces the concentration of the SCN^- to only a slight extent.

Dilute a little $FeSO_4$ solution and add potassium ferricyanide solution, $K_3Fe(CN)_6$ (E). What is the trade-name of the precipitate?

Add a little potassium ferrocyanide solution, $K_4Fe(CN)_6$, to some $FeCl_3$ solution (E).

How could one test for Fe^{+++} and Fe^{++} in a solution containing both?

5. *Precipitation of Iron Sulfide.*—Prepare some colorless ammonium sulfide solution, $(NH_4)_2S$, by saturating some NH_4OH with H_2S. Add a little of this reagent to some $FeSO_4$ solution (E). See if FeS is readily soluble in dilute acids, like HCl (E).

Note.—The precipitate obtained when $NH_4OH + H_2S$ is added to a ferric solution seems to be Fe_2S_3, and not FeS, as it is sometimes represented. Fe_2S_3 is black, and has the general properties of FeS.

(47) Nickel, Ni^{++}. 1. *The Nickel-ammonia Complex.*—Dilute 2 cc. of nickel nitrate solution, $Ni(NO_3)_2$, and add NH_4OH, at first drop by drop (E), and then in excess (E). Label the products with their colors.

Note.—The general rule for the composition of metal-ammonia complex ions is that the number of NH_3 molecules is twice the valence of the metal; *e.g.*, $Ag(NH_3)_2^+$, $Cu(NH_3)_4^{++}$, $Co(NH_3)_6^{+++}$, etc. Divalent nickel and cobalt are exceptions in that they form several complexes, the most common of them containing six NH_3 molecules; *e.g.*, $Ni(NH_3)_6^{++}$ and $Co(NH_3)_6^{++}$.

2. *Insolubility of Nickel Sulfide in Hydrochloric Acid.*—Acidify some dilute $NiCl_2$ solution with dilute HCl, and saturate with H_2S (?). Now neutralize the free acid with NH_4OH, resaturating with H_2S, if necessary. Write the equation for the reaction between $NiCl_2$ and $(NH_4)_2S$. Filter, transfer the precipitate to a test tube, and try to dissolve it in dilute HCl (?). Add a little HNO_3 to the HCl-NiS mixture and warm (E).

Note.—It is rather anomalous that HCl should prevent the precipitation of NiS, and yet NiS should be insoluble in HCl. Some authorities consider that NiS is really soluble, but that the action is *very slow*.

3. *Colloidal Nickel Sulfide.*—To a little $Ni(NO_3)_2$ solution add yellow ammonium sulfide solution, $(NH_4)_2S_x$ (desk). Try to filter out the precipitate (?). Which appears to be the proper precipitant for NiS, $NH_4OH + H_2S$ or $(NH_4)_2S_x$? The brown precipitate may be coagulated and made filterable by acidifying the mixture with $HC_2H_3O_2$ and boiling.

4. *Action of Sodium Peroxide on Nickelous Hydroxide.*—Add NaOH solution to a little dilute $Ni(NO_3)_2$ solution in a small beaker (E). To this mixture add Na_2O_2 slowly, with stirring. Does the Na_2O_2 produce any apparent effect?

5. *The Dimethylglyoxime Reaction.*—To a little dilute $Ni(NO_3)_2$ solution add very dilute NaOH solution very carefully until, on shaking, the precipitate just fails to dissolve. Dissolve the precipitate in a little $HC_2H_3O_2$. To this practically neutral solution add a few drops of dimethylglyoxime solution (storeroom) (?). (SEPARATION OF Ni^{++} FROM Co^{++}.) Divide the mixture, and test the solubility of the precipitate in HCl and in NH_4OH (?).

(**48**) **Cobalt, Co^{++}.** 1. *The Cobalt-ammonia Complex.*—To a dilute cobalt nitrate solution, $Co(NO_3)_2$, add NH_4OH slowly, noting two stages in the reaction (E's). Compare Ni^{++}, (**47**, 1). Reserve the solution for the next experiment.

2. *Properties of Cobalt Sulfide.*—Saturate the solution from the preceding experiment with H_2S (E). (Consider the reaction as between $Co(NO_3)_2$ and $(NH_4)_2S$.) Filter and try the solubility of the precipitate in dilute HCl (?), in dilute aqua regia (?). Compare NiS, (**47**, 2).

3. *Oxidation of Cobaltous Hydroxide by Sodium Peroxide.*—To some dilute $Co(NO_3)_2$ solution in a small beaker add NaOH solu-

tion (E). To the mixture containing the $Co(OH)_2$ add Na_2O_2 as in (**47**, 4). In this respect does Co resemble Fe or Ni? Boil, allow the precipitate to settle, and wash by decantation. Dissolve the residue in dilute HCl (E), warm, and test the vapors evolved with litmus paper (?).

4. *The Dimethylglyoxime Reaction.*—To a dilute $Co(NO_3)_2$ solution add very dilute NaOH and $HC_2H_3O_2$ as in (**47**, 5). Now add a few drops of dimethylglyoxime solution (storeroom). What is the color of the solution?

5. *The Vogel Reaction.*—To a little concentrated $Co(NO_3)_2$ solution add 1 or 2 cc. of NH_4SCN solution and a little amyl-alcohol-ether mixture, and shake. The blue-green color is due to $(NH_4)_2Co(SCN)_4$, easily soluble in the alcohol-ether layer. Dilute the mixture with 1 or 2 volumes of water and shake thoroughly (?). What is the necessary condition for the use of this test?

***(49) Complication by Phosphates and Oxalates.**[1] 1. *Precipitation of Group IV Ions and Mg^{++} in Group III.*—Dissolve a pinch of calcium phosphate, $Ca_3(PO_4)_2$, in dilute HCl, and add NH_4OH, as in the precipitation of Group III (?). What is the precipitate? In what group is Ca^{++} normally precipitated?

Exercises

1. What members of Group III could be present in a solution containing free NH_4OH?
2. What members of Group III form amphoteric hydroxides?
3. Using NH_4OH, how could $Cr_2(SO_4)_3$ and $NiSO_4$ be distinguished?
4. What two members of Group III are precipitated by the group reagent as hydroxides? What is their valence?
5. What members of Group III are absent if NH_4OH gives no reaction (precipitate or color) with the H_2S-free solution?
6. What hydroxides of Group III are oxidized by Na_2O_2 in alkaline solution? What hydroxides (or oxides) are reduced by H_2O_2 in acid solution?

[1] As stated in (**33**, footnote), experiments and procedures marked with an asterisk may be omitted at the discretion of the instructor without in any way involving the continuity of the regular analytical scheme. For example, procedures (**49**), (**56**), and (**57**) may be omitted in courses which do not include unknowns containing phosphates and oxalates of the alkaline earth metals and magnesium without any complications at all. The student should consult with the instructor with regard to all omissions.

7. How would one proceed to separate the ions, Al^{+++}, Zn^{++}, and Ni^{++}, by means of NaOH and NH_4OH?
8. What reagent will separate NiS and FeS in one step?
9. What members of this group form black sulfides?
10. What cation of this group gives with NH_4OH a white precipitate soluble in excess of the reagent?
11. What members of this group form NH_3 complexes?
12. Refer to the Table of Solubilities (pages 122–125) and find a cation belonging to a group subsequent to Group III which forms a sulfide insoluble in water. Why is not this ion a member of Group III?
13. What non-metallic substance resembling $Al(OH)_3$ is sometimes met in this group? How may it be distinguished from $Al(OH)_3$?
14. Why is $Mn(OH)_2$ not precipitated by NH_4OH in the presence of NH_4^+?
15. What members of this group form sulfides insoluble in dilute HCl?
16. What ion gives no reaction with NH_4OH in the presence of NH_4Cl, but upon standing in contact with air develops a brown precipitate?
17. Why should yellow ammonium sulfide, $(NH_4)_2S_x$, never be used in the analysis of Group III?
18. A solution is known to be either $Al_2(SO_4)_3$ or $ZnSO_4$. What test should be made?
19. Indicate reagents and products (see page 23 for form in answers) in the following one-step separations: (*a*) $Al(NO_3)_3$ and $Zn(NO_3)_2$, (*b*) $Cr(OH)_3$ and $Fe(OH)_3$, (*c*) $Co(NO_3)_2$ and $Mn(NO_3)_2$, (*d*) $ZnCl_2$ and $NiCl_2$, (*e*) CoS and FeS, (*f*) H_2SiO_3 and $Al(OH)_3$, (*g*) MnO_2 and asbestos, (*h*) $Fe(OH)_3$ and $Ni(OH)_2$, (*i*) Na_2CrO_4 and $Zn(C_2H_3O_2)_2$.
20. Which is the more powerful oxidizing agent, permanganic acid or PbO_2 in the presence of HNO_3?
21. Do the trivalent metals form carbonates? Why?
22. Normal solutions of HCl and $HC_2H_3O_2$ are saturated with H_2S. Compare the concentrations of the S^{--} ions in the two cases.
23. Explain why the addition of a soluble acetate increases the S^{--} concentration in acid solutions containing H_2S.
24. A Group III solution gives with NH_4OH a deep-blue solution over a red-brown precipitate. What ions are indicated?
25. Apply the rules of hydrolysis to NH_4AlO_2 and $FePO_4$.
26. State what, if anything, would be formed in the following cases (do not balance equations):

(*a*) $K_2Cr_2O_7 + HCl + H_2S$.
(*b*) $FeCl_3 + H_2S$.
(*c*) $CrCl_3 + Na_2CO_3$ solution.
(*d*) $Zn(NH_3)_4SO_4 + H_2SO_4$.
(*e*) $ZnCl_2 + NaC_2H_3O_2 + H_2S$.
(*f*) $Fe(OH)_3 + NaOH$ solution.
(*g*) $Mn(OH)_2$ + air.
(*h*) MnO_2 + concentrated HNO_3.
(*i*) $KMnO_4 + Pb(NO_3)_2$.

(*j*) $FeCl_3 + K_4Fe(CN)_6$.
(*k*) $(NH_4)_2Co(SCN)_4$ in ether + H_2O.
(*l*) $Ni(OH)_2 + Na_2O_2$.

27. Criticize the following definition of Group III: "Group III contains those cations whose sulfides (or hydroxides) are insoluble in water, but soluble in dilute acids."

ANALYSIS

(50) Precipitation.—If the solution is an unknown on Group III only, add 10 cc. of NH_4Cl solution, heat to boiling, and add NH_4OH in slight excess (litmus test); if the solution is a filtrate from the precipitation of Group II, boil until H_2S is expelled (test the vapors with a piece of filter paper moistened with lead acetate solution, $Pb(C_2H_3O_2)_2$), and add to the hot solution NH_4OH in slight excess (litmus test). A precipitate may contain Al, Cr, Fe, Mn, Ba, Sr, Ca, and Mg as hydroxides, phosphates, and oxalates.[1] Without filtering, saturate the mixture with H_2S, heat nearly to boiling, and stir well (to coagulate the precipitate). Filter and test the filtrate for the completeness of the reaction by adding a little NH_4OH and saturating again with H_2S. If more precipitate forms, heat the mixture and filter through a fresh paper. Wash precipitates *at once* with warm water, adding the first washings to the main filtrate. Reserve this combined filtrate for (**64**). Treat the precipitate (or precipitates) by (**51**).

Notes.—1. The filtrate from Group II already contains NH_4Cl in sufficient amount to prevent the precipitation of ordinary amounts of $Mg(OH)_2$, $Ca(OH)_2$, etc. This was formed by the neutralization of the 4 cc. of dilute HCl added in the precipitation of Group I by the NH_4OH added above.

2. The H_2S from the Group II precipitation is boiled out, so that the effect of NH_4OH alone on the solution may be noted. Considerable time may be saved by taking advantage of the information obtained in this way.

3. The appearance of all precipitates or solutions should be closely observed, since the colors indicate the presence or absence of certain members of the group.

4. Yellow ammonium sulfide, $(NH_4)_2S_x$, must not be used in the analysis of Group III, because of its solvent action on NiS. $NH_4OH + H_2S$ is used instead.

5. A brown filtrate from (**50**) is due to a colloidal suspension of NiS in $(NH_4)_2S_x$, which may have been erroneously used or else formed by oxida-

[1] Borates and fluorides might also precipitate certain members of Group IV, but these ions presumably have been removed by the HNO_3 evaporation in (**26**).

tion of colorless $(NH_4)_2S$. This brown solution may be taken as a very conclusive test for Ni^{++}. The NiS should be precipitated by acidifying with $HC_2H_3O_2$ and boiling the mixture, and the clear filtrate reserved for (**64**).

6. If moist sulfides are allowed to stand in contact with air, some sulfate will be formed by oxidation and will dissolve in the wash water. For this reason, the precipitate should be washed promptly with hot (free from dissolved air) water.

(51) Separation of the Aluminium and Iron Subgroups.—Transfer the precipitate on the filter papers from (**50**) to a beaker and add 10 cc. of water. Then add, with stirring, cold dilute HCl as long as there is any apparent action. If a black residue remains (suggesting what substances?), add, without filtering, a few drops of concentrated HNO_3 and heat to boiling. If the action is not complete, as shown by the residue remaining black, add more HCl and a few more drops of HNO_3 and heat again. Dilute with about 10 cc. of water, filter, and wash the residue, adding the first washings to the main filtrate. Reject the residue (sulfur). Evaporate the solution to about 10 cc. in a small Pyrex beaker to remove excess of acids. Dilute to about 15 cc., and add NaOH solution slowly, with stirring, as long as the precipitate appears either to form or to dissolve, carefully avoiding unnecessary excess of NaOH. Cool the mixture and add solid Na_2O_2 (storeroom) slowly, with stirring, as long as the yellow color deepens. If phosphates and oxalates may be present, add 5 cc. of Na_2CO_3 solution to convert Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} into insoluble carbonates. Boil for 3 or 4 minutes to decompose the excess of Na_2O_2, and then dilute with an equal volume of water. If no precipitate forms, the Iron Subgroup is absent; analyze the solution by (**52**). A colored precipitate indicates the presence of the Iron Subgroup; analyze it by (**55**) and the filtrate by (**52**). A pure white precipitate indicates the absence of the Iron Subgroup, but the presence of Group IV or Mg^{++}; filter, wash, and analyze the solution by (**52**). Dissolve the precipitate in dilute HCl, and analyze it for Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} by (**64**) and subsequent procedures.

Notes.—1. The purpose of adding the Na_2CO_3 is to convert any $BaCrO_4$ and $SrCrO_4$ into $BaCO_3$ and $SrCO_3$. Otherwise the Cr would be carried into the Iron Subgroup as insoluble chromates.

2. Proper observation and interpretation of the colors of the precipitates and solutions formed will not only indicate the presence or absence of certain

ions, but will also suggest, in many cases, how the procedure may be shortened without risk of error.

TABLE VII.—PRECIPITATION OF GROUP III AND SEPARATION OF ALUMINIUM AND IRON SUBGROUPS

(50) Solution: Filtrate from Group II or unknown in Group III only. If filtrate from Group II, boil to expel H_2S; if not, add 10 cc. NH_4Cl solution and omit boiling. Add NH_4OH. Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_{2-3}$; also Al, Cr, Fe, Mn, Ba, Sr, Ca, and Mg as phosphates and oxalates if these ions are present. Solution: Mn^{++}, and Zn^{++}, Ni^{++} and Co^{++} as NH_3 complexes. Without filtering, saturate with H_2S. Filter, wash, precipitate.		
Precipitate: $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, NiS, CoS; also Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} as phosphates and oxalates. (51) Add HCl. Dissolve any black residue (NiS, CoS) by adding HNO_3 to the HCl mixture and boiling. Filter out any S. Add NaOH, Na_2O_2, and Na_2CO_3 solution (if phosphates and oxalates are present). Boil, dilute, filter, and wash precipitate.		Filtrate: Groups IV, V. (See Tables XI or XII)
Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2. (See Table VIII)	Precipitate: MnO_2, $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_3$; Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} as carbonates, phosphates, and oxalates. (See Tables IX, X)	

(52) **Aluminium.**—To the solution from (51) add dilute HNO_3 to acidity (litmus test), and then NH_4OH to alkalinity (litmus test). If a white precipitate forms, carefully add excess of NH_4OH (3 to 5 cc., usually) as long as any of the precipitate appears to redissolve. Heat just to boiling. Filter out any precipitate and wash it with very dilute warm NH_4Cl solution, reserving the filtrate for (53). The precipitate is probably $Al(OH)_3$.

If the precipitate is small, it may be silicic acid, H_2SiO_3, introduced as an impurity in the various alkaline reagents used. In such a case, pour a few cubic centimeters of hot dilute HCl through the paper, and evaporate the filtrate *just to dryness* in a small Pyrex beaker. Cool, and to the residue add 5 cc. of water and 1 or 2 cc.of dilute HCl, warm, and filter. To the filtrate add 1 drop of aurin tricarboxylic acid and an excess of *clear*

NH_4OH, and heat to boiling. The formation of a precipitate which absorbs the red dye, leaving a comparatively colorless filtrate, indicates Al^{+++}.

(**53**) **Chromium.**—Carefully neutralize the ammoniacal filtrate from (**52**) with $HC_2H_3O_2$ (litmus test). If the solution shows a yellow-to-orange tint,[1] Cr is present as $Cr_2O_7^{--}$. In that case proceed at once to (**54**). If the color of the solution is not conclusive, take a small portion of it, add a few drops of dilute H_2SO_4, about 2 cc. of ether, and 2 cc. of H_2O_2 solution, and shake promptly. A blue color in the ether layer indicates the presence of $Cr_2O_7^{--}$. Reserve the remainder of the solution for (**54**).

(**54**) **Zinc.**—To the solution from (**53**) add 2 or 3 drops of $K_4Fe(CN)_6$ solution. A white precipitate of $Zn_2Fe(CN)_6$ indicates Zn^{++}.

Note.—A large excess of $K_4Fe(CN)_6$ is avoided, since it reacts with dichromates, giving a reddish color, which more or less obscures the test.

TABLE VIII.—ANALYSIS OF ALUMINIUM SUBGROUP

(**52**) Solution: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2. Add HNO_3, excess of NH_4OH, heat to boiling, filter.

Precipitate: $Al(OH)_3$, H_2SiO_3 (as impurity). Filter, wash, and pour warm dilute HCl through filter. Evaporate filtrate just to dryness. Take up in HCl, filter, add 1 drop of alizarine solution and excess NH_4OH. Heat to boiling. Red precipitate: $Al(OH)_3$.	Filtrate: Na_2CrO_4 (yellow), $Zn(NH_3)_4^{++}$. (**53**) Add $HC_2H_3O_2$. Solution: $Na_2Cr_2O_7$ (orange), $Zn(C_2H_3O_2)_2$. Yellow-orange color indicates $Cr_2O_7^{--}$; proceed to (**54**). If color is not conclusive, divide, reserving larger portion for (**54**). To smaller portion add dilute H_2SO_4, ether, H_2O_2. Shake promptly. Blue color in ether indicates $Cr_2O_7^{--}$.

(**54**) Solution: $Na_2Cr_2O_7$, $Zn(C_2H_3O_2)_2$. Add $K_4Fe(CN)_6$. Precipitate: White $Zn_2Fe(CN)_6$.

(**55**) **Manganese.**—Transfer the residue from (**51**) (which may contain MnO_2, $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_3$, and possibly Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} as phosphates, oxalates, or car-

[1] A yellow solution may appear colorless by artificial light.

bonates) to a porcelain evaporating dish or casserole,[1] add 10 to 20 cc. of concentrated HNO_3, and heat to boiling. A black residue, insoluble in HNO_3, is MnO_2 or $Co(OH)_3$, or both. In case of such a residue, slowly add to the boiling mixture (under a hood, if one is available) sodium nitrite solution, $NaNO_2$, from a test tube, until all the precipitate is dissolved. Continue the boiling, and after the brown fumes are expelled, add about 1 gram of solid $KClO_3$, a little at a time, with stirring, and boil gently for 2 or 3 minutes. A brown-black residue is MnO_2. Filter off any precipitate by means of an asbestos filter prepared as follows (Instructions): Place a small plug of glass wool in the apex of a funnel, and pour over it a suspension of asbestos in water until a layer of asbestos about 5 mm. thick is formed in the funnel; wash with water until the filtrate is clear. Wash the precipitate on the asbestos filter with hot water, combining the washings with the original filtrate. Reserve this solution for (**56**).

If the precipitate is small, the presence of Mn should be confirmed as follows: Scrape off the dark surface of the asbestos filter with a spatula and transfer it to a small beaker. Add 1 or 2 grams of PbO_2, and about 10 cc. of dilute HNO_3, and boil for about 2 minutes. Allow the solid materials to settle and decant the solution into a test tube. A pink-red color is due to MnO_4^-.

(**56**) **Phosphates and Oxalates.**—If phosphates and oxalates are known to be absent, proceed directly to (**57***a*). If phosphates and oxalates may be present, test a small portion of the filtrate from (**55**) for PO_4^{---}, reserving the main portion for (**57***b*), and a small sample of the *original* substance for $C_2O_4^{--}$, using the following tests:

Phosphate.—Add to 2 cc. of the solution 3 or 4 cc. of $(NH_4)_2MoO_4$ solution and heat to boiling. A yellow precipitate indicates the presence of PO_4^{---}.

Oxalate.—Acidify a small sample of the *original* substance with dilute H_2SO_4 and boil to decompose carbonates. Place a little MnO_2 in a test tube fitted with a thistle tube and a delivery tube (see "Anion Analysis" (**90**, 2), page 81), and introduce the solution through the thistle tube. Warm, and pass any gas

[1] A black precipitate may be seen more readily in a porcelain vessel than in a beaker.

formed through $Ca(OH)_2$ solution. A milky-white precipitate indicates the presence of $C_2O_4^{--}$.

Note.—The test for oxalate is made on the original substance instead of the filtrate from (**55**), because (1) oxalates may have been removed to a greater or less extent by oxidation to carbonates by the $NaOH$-Na_2O_2 treatment, and (2) oxalates in the presence of Mn^{++} and Co^{++} are completely oxidized to CO_2 by the HNO_3-$KClO_3$ treatment. It should be clearly understood, however, that the oxalate ion was not removed in time to prevent its precipitation of such ions as Ba^{++}, Sr^{++}, and Ca^{++} along with Group III.

If either phosphate or oxalate is found, proceed to (**57***b*); if both are absent, proceed to (**57***a*).

(**57***a*) **Iron in the Absence of Phosphate and Oxalate.**—Neutralize the HNO_3 filtrate from (**56**) with NH_4OH (litmus test), and then add 5 cc. excess of NH_4OH. Filter and wash the precipitate. A reddish-brown precipitate is $Fe(OH)_3$, which may be further confirmed as a test for Fe by dissolving it in dilute HCl and adding NH_4SCN solution. A red color, which is not bleached out by boiling, is due to $Fe(SCN)_3$.

Note.—If nitrates were not completely washed out of the NH_4OH precipitate, a little HNO_3 may be present, which will give a faint-red color with NH_4SCN. This red color, however, is completely destroyed by boiling. The student should keep in mind the fact that nitrates in acid solution give a red color frequently mistaken for a test for Fe^{+++}.

Acidify the filtrate from the $Fe(OH)_3$ precipitate with $HC_2H_3O_2$, and divide into two portions. Test one portion for Ni^{++} by (**58**) and Co^{++} by (**59**).

* (**57***b*) **Iron in the Presence of Oxalate and Phosphate.**—Classify the solution under *A* or *B*, and proceed as directed.

Note.—If both $C_2O_4^{--}$ and PO_4^{---} are present, use both A and B.

A. Oxalate Present.—If Mn^{++} was not found in (**55**), remove $C_2O_4^{--}$ by adding a little MnO_2 to the solution and boiling, slowly adding solid $KClO_3$ as in (**55**). Filter on an asbestos filter, wash with a little water, and reject the precipitate. If Mn^{++} was present, this paragraph may be omitted.

Note.—Oxalic acid is very readily oxidized to CO_2 and H_2O by MnO_2 in warm acid solution. It appears remarkably resistant to a great many

oxidizing agents, being oxidized only slowly by such powerful agents as concentrated HNO_3, aqua regia, and $HClO_3$.

If PO_4^{---} is present, proceed to *B*; if absent, test for Fe^{+++} according to (**57***a*), reserving filtrate for *C*.

B. Phosphate Present.—Test one-tenth of the filtrate (reserving the larger portion for the next paragraph) for Fe^{+++} by adding 2 or 3 cc. of concentrated HCl and evaporating almost to dryness, preferably in a casserole held in the hand.[1] Take up the residue in 10 cc. of water and a few drops of dilute HCl and add NH_4SCN solution. A permanent red color, not bleached out by boiling, indicates the presence of Fe^{+++}.

To the main portion of the solution add NH_4OH slowly, until a precipitate which will not redissolve on stirring just forms. Dissolve the precipitate in the smallest amount of $HC_2H_3O_2$, and add 5 cc. of 50 per cent $NH_4C_2H_3O_2$ solution. If the mixture is not reddish-brown, add $FeCl_3$ solution slowly until such a color is obtained. Boil gently for 3 minutes in a 300-cc. beaker. Filter while still hot. To the filtrate add NH_4OH to decided alkalinity and boil again. Reject all precipitates.

Note.—The purpose of the above procedure is the separation of PO_4^{---} from the divalent cations, Ni^{++}, Co^{++}, Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++}. This is accomplished by precipitating it as $FePO_4$, which is very insoluble in neutral solutions. After testing for Fe^{+++}, excess of $FeCl_3$ is added to the remainder of the solution, and then excess of $NH_4C_2H_3O_2$. Upon boiling, $FePO_4$ is precipitated, and next the remainder of the Fe^{+++} is thrown down as basic ferric acetate, $Fe(OH)_2C_2H_3O_2$. The acetates of the divalent cations, on the other hand, are not hydrolyzed like $Fe(C_2H_3O_2)_3$, and hence are left in the solution.

C. Separation of Nickel and Cobalt from Groups IV and V.—Saturate the ammoniacal solution from *B* with H_2S, filter, and wash the precipitate. Combine the washings with the main filtrate and reserve for the next paragraph. Dissolve the precipitate by pouring over the filter hot dilute aqua regia, wash once, adding the washings to the main filtrate. Make the combined filtrate alkaline with NH_4OH, then acid with $HC_2H_3O_2$, and divide into two equal parts. Test one portion for Ni^{++} by (**58**), and the other from Co^{++} by (**59**).

[1] This procedure converts nitrates into chlorides, and is necessary, since HNO_3 gives a red color with NH_4SCN, vitiating the test for Fe^{+++}.

Evaporate the filtrate from the H_2S precipitation in the preceding paragraph to dryness, add 5 cc. of concentrated HNO_3, and evaporate again. Finally, ignite the residue very gently as long as a gas seems to be given off.[1] Take up this residue in 10 cc. of water acidified with 2 cc. of dilute HCl, warm, and filter, if necessary. Test this solution for Group IV and Mg^{++} by (**64**) and subsequent procedures.

(**58**) **Nickel.**—To one portion of the solution from (**57**) add dimethylglyoxime solution (storeroom). A red precipitate indicates Ni^{++}, and a brown solution (or filtrate) indicates Co^{++}.

(**59**) **Cobalt.**—Evaporate the second portion of the solution from (**57**) to 1 or 2 cc. in a Pyrex beaker or evaporating dish, add an equal volume of NH_4SCN solution, and 1 or 2 cc. of amyl alcohol-ether mixture. Shake vigorously. A blue-to-green color in the alcohol-ether layer indicates Co^{++}.

TABLE IX.—ANALYSIS OF IRON SUBGROUP
(Phosphates and Oxalates Absent)

(**55**) Residue: MnO_2, $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_3$. Add concentrated HNO_3 and boil. Add $NaNO_2$ solution to dissolve any black residue. To boiling solution add solid $KClO_3$. Filter on asbestos, wash precipitate.

Residue: MnO_2. Add PbO_2, dilute HNO_3, boil. Solution: Purple $HMnO_4$.	(**57***a*) Filtrate: Fe^{+++}, Ni^{++}, Co^{++} as nitrates. Dilute, add NH_4OH in excess, filter, wash precipitate.		
	Precipitate: Red $Fe(OH)_3$. Dissolve in dilute HCl, add NH_4SCN. Solution: Red $Fe(SCN)_3$.	Filtrate: $Ni(NH_3)_6^{++}$, $Co(NH_3)_6^{++}$ as nitrates. Acidify with $HC_2H_3O_2$, divide.	
		(**58**) To one portion add dimethylglyoxime. Precipitate: Red Ni-dimethylglyoxime. Brown solution: Co-dimethylglyoxime.	(**59**) Evaporate second portion, add NH_4SCN, amyl alcohol-ether mixture, shake vigorously. Blue-green layer indicates Co.

[1] The purpose of this treatment is to convert all ammonium salts into NH_4NO_3, which is decomposed into N_2O and H_2O by the subsequent ignition. Unless removed in this way, a large amount of ammonium salts may completely prevent the precipitation of Group IV in (**64**). *Cf.* (**64**, note 1).

TABLE X.—ANALYSIS OF IRON SUBGROUP
(Phosphates and Oxalates Present)

(**55**) Residue: MnO_2, and Fe^{+++}, Ni^{++}, Co^{+++}, Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} as hydroxides, phosphates, oxalates, and carbonates. Add concentrated HNO_3 and boil. Add $NaNO_2$ solution to dissolve any black residue. To boiling solution add solid $KClO_3$. Filter on asbestos, and wash precipitate.

Residue: MnO_2.
Add PbO_2, dilute HNO_3, boil.
Solution: Purple $HMnO_4$.

(**56**) Filtrate: Fe^{+++}, Ni^{++}, Co^{++}, Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}. Test a small portion of the solution for PO_4^{---} by $(NH_4)_2MoO_4$ and a small portion of the original for $C_2O_4^{--}$ by MnO_2, H_2SO_4, and $Ca(OH)_2$.

A. *Oxalate Present.*—(**57***b*) If Mn^{++} was absent, add to solution MnO_2 and boil, and reprecipitate MnO_2 by adding solid $KClO_3$ to boiling solution. Filter, reject precipitate. If PO_4^{---} is present, proceed to B; if absent, test for Fe^{+++} by (**57***a*), reserving filtrate for C.

B. *Phosphate Present.*—Use the solution free from $C_2O_4^{--}$. Add to one-tenth concentrated HCl, evaporate, add water, HCl, and NH_4SCN. Red color, $Fe(SCN)_3$ indicates Fe^{+++}. Add $FeCl_3$ to give excess Fe^{+++}, then NH_4OH, $HC_2H_3O_2$, $NH_4C_2H_3O_2$. Boil, filter, wash precipitate.

Precipitate: $FePO_4$, $Fe(OH)_2C_2H_2O_2$.
Discard.

C. Solution: Ni^{++}, Co^{++}, Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, NH_4^+. Saturate with H_2S, filter, wash precipitate.

Precipitate: NiS, CoS. Dissolve in dilute aqua regia, filter out S, evaporate. Add NH_4OH, $HC_2H_3O_2$, and divide.

(**58**) To one portion add dimethylglyoxime.
Precipitate: Red Ni-dimethyl glyoxime.
Solution: Brown Co-dimethyl glyoxime.

(**59**) Evaporate second portion, add NH_4SCN, amyl alcohol-ether mixture, and shake vigorously.
Blue-green layer indicates Co^{++}.

Filtrate: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, NH_4^+.

Evaporate to dryness, add conc. HNO_3, ignite.
Residue: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}. Add H_2O, HCl, and proceed to (**64**).

GROUP IV. THE AMMONIUM CARBONATE GROUP

This group contains the ions of the alkaline earth[1] metals, Ba^{++}, Sr^{++}, and Ca^{++}. The chlorides of these metals are soluble in water, and their sulfides and hydroxides are not precipitated in the presence of ammonium salts.

[1] The term "alkaline earths" was originally applied to lime, CaO, and magnesia, MgO. Later, strontia, SrO, and baryta, BaO, were discovered and included under this name. There is at present a tendency to limit the use of the term to the oxides of calcium, strontium, and barium.

The following table (compiled from data in Landolt-Börnstein's Tabellen) shows the solubility in *moles per liter* of the compounds which are involved in the separation and analysis of the group:

SOLUBILITY TABLE

	Ba^{++}	Sr^{++}	Ca^{++}	Mg^{++}
CO_3^{--}	0.00012	0.000074	0.00013	0.01
CrO_4^{--}	0.000015	0.0059	1	3
SO_4^{--}	0.00001	0.0004	0.015	2.8
$C_2O_4^{--}$	0.00038	0.00024	0.00004	0.0027
$(OH)_2^{--}$	0.22000	0.065	0.022	0.0001

It will be seen from this table that the carbonate is the most uniformly insoluble salt of these metals. Hence, the group is precipitated as carbonates. The fact that Mg^{++} is not also precipitated is due to the fact that $MgCO_3$ is readily soluble in ammonium salts, which have been introduced during the analysis, particularly in neutralizing the filtrates from Groups II and III.

Precipitation of Ba^{++} as $BaCrO_4$ appears the most promising way to separate Ba^{++} from Sr^{++} and Ca^{++}. No direct means of separating Sr^{++} and Ca^{++} is suggested by the table, since the solubilities of their salts are either too large, or else lie too close together. Ca^{++} forms a very insoluble precipitate with $K_4Fe(CN)_6$ and, as will be seen later, this reaction may be used to effect a separation from Sr^{++}. Usually an indirect method is used. Sr^{++} is tested for in the presence of Ca^{++} by saturated $CaSO_4$ solution; then most of the Sr^{++} and some of the Ca^{++} are removed by precipitation by $(NH_4)_2SO_4$ solution. The filtrate may be considered a saturated solution of both $SrSO_4$ and $CaSO_4$. From the table it will be seen that there is not much difference in the molar solubilities of $SrSO_4$ and SrC_2O_4, while CaC_2O_4, because of its lower solubility, should be easily precipitated from saturated $CaSO_4$ solution.

PRELIMINARY EXPERIMENTS

(60) Precipitation of the Group.—Dilute 2 or 3 cc. of barium nitrate solution, $Ba(NO_3)_2$ (used as a representative of this group), to 10 cc., heat to boiling, and add ammonium carbonate

solution, $(NH_4)_2CO_3$ (E). Allow the mixture to stand 15 minutes in order to complete the precipitation. Decant, and try the solubility of the precipitate in 5 cc. of hot acetic acid, $HC_2H_3O_2$.

Note.—Contrary to the probable opinion of the student at this point, chemical reactions in solutions are by no means instantaneous. It is characteristic of the precipitates of this group to form slowly, especially from dilute solutions. Heating and shaking may hasten such reactions to some extent, but the wiser policy is always to allow the mixtures to stand until the precipitation is complete; that is, the precipitate is "digested" (see page xi) in the solution. Heating such a digestion mixture favors the formation of large-grained particles, which are more easily filtered, and is very valuable in this way. Instead of waiting for these slow reactions to complete themselves, the student should proceed with other work; for example, the preliminary experiments on Group V.

(**61**) **Barium, Ba^{++}.** 1. *Reaction with Calcium Sulfate Solution.*—Dilute 1 cc. of $Ba(NO_3)_2$ solution to 10 cc., and add a little clear saturated calcium sulfate solution, $CaSO_4$ (E). Does the precipitate form immediately? *Cf.* (**62**, 1).

2. *Precipitation of Barium Chromate.*—Dilute 2 cc. of $Ba(NO_3)_2$ solution to about 20 cc. in a small beaker, and add $K_2Cr_2O_7$ solution in excess (E). (Separation of Ba^{++} from Sr^{++} and Ca^{++}.) Heat to boiling, filter, and divide the filtrate into two parts. To one part add a little $CaSO_4$ solution and compare with the other part (?). Was the original precipitation complete?

To the second portion add 5 cc. of sodium acetate solution, $NaC_2H_3O_2$, boil and filter. What is the precipitate? Write the equation for the reaction between $Ba(NO_3)_2$ and $K_2Cr_2O_7$ as reversible, and tell what product is removed by the $C_2H_3O_2^-$ ion of the $NaC_2H_3O_2$ (?). Heat the mixture to boiling, filter, and divide the filtrate. To one part add $CaSO_4$ solution, and compare with the other part. Was the precipitation complete in the presence of the $NaC_2H_3O_2$?

3. *Flame Test.*—Clean a platinum wire[1] by dipping it into concentrated HCl in a test tube (Not in the reagent bottle!

[1] A piece of platinum wire about 6 cm. long is sealed into the end of a short piece of glass tubing (Instructions). A good way to protect the wire against rough usage in the drawer of the desk is to insert the glass tubing into a perforated cork and keep it in a 10-cm. test tube as shown in the figure.

Fig. 7.—Platinum wire in test tube.

Why?) and heating it in the non-luminous Bunsen flame. Repeat until the wire gives practically no color to the flame. Then dip in a little $BaCl_2$ or $Ba(NO_3)_2$ solution, and heat in the flame (?).

Notes.—1. The flame coloration is much more conspicuous if the wire is held horizontally in the outer cone near the base of the flame, and the "layer" of coloration observed "edgewise."

2. The flame coloration is due to *gaseous* $BaCl_2$ or $Ba(NO_3)_2$. Non-volatile barium compounds give little or no flame reaction.

(62) Strontium, Sr^{++}. 1. *Reaction with Calcium Sulfate Solution.*—Dilute 1 cc. of strontium nitrate solution, $Sr(NO_3)_2$, to about 5 cc., and add a few cubic centimeters of saturated $CaSO_4$ solution (E). Shake and warm, if necessary. Note the difference in the speeds of precipitation of $BaSO_4$ and $SrSO_4$ (?)

2. *Flame Test.*—Make the flame test on a little $Sr(NO_3)_2$ solution (?).

3. *Relative Solubilities of Sulfate and Oxalate.*—To some dilute $Sr(NO_3)_2$ solution add $(NH_4)_2SO_4$ solution in excess (E). (PARTIAL SEPARATION OF Sr^{++} FROM Ca^{++}.) Shake, warm, allow to stand 10 minutes, and filter. The filtrate may be considered a saturated solution of $SrSO_4$. Add to it a few drops of ammonium oxalate solution, $(NH_4)_2C_2O_4$ (?). Does SrC_2O_4 appear to be much more insoluble than $SrSO_4$?

4. *Solubility of Strontium Ferrocyanide.*—Dilute 1 cc. of $Sr(NO_3)_2$ with several volumes of water, and add 1 cc. of NH_4Cl solution and a few drops of potassium ferrocyanide solution, $K_4Fe(CN)_6$(?). Compare with the reaction with Ca^{++} in (**63,** 3).

(63) Calcium, Ca^{++}. 1. *Relative Solubility of Sulfate and Oxalate.*—Dilute 2 cc. of calcium chloride solution, $CaCl_2$, to 10 cc., and add ammonium sulfate solution, $(NH_4)_2SO_4$, in slight excess. Shake well and allow the mixture to stand for 10 or 15 minutes for the reaction to complete itself (E). Filter, and add NH_4OH to alkalinity, and then a few drops of $(NH_4)_2C_2O_4$ solution (E). Is Ca^{++} completely precipitated by sulfates? (See table, page 54.) Try the solubility of the CaC_2O_4 precipitate in $HC_2H_3O_2$ (?), then in HCl (E).

Note.—The solubility of CaC_2O_4 in HCl, and insolubility in $HC_2H_3O_2$, is due to the differences in strength (that is, degree of ionization) in the acids

involved. Solutions of these acids containing one-tenth mol per liter are ionized as follows: HCl 86, $H_2C_2O_4$ 17, $HC_2H_3O_2$ 1.3 per cent. Now CaC_2O_4 is very slightly soluble in water, and the dissolved portion ionizes, probably to a considerable degree. The condition may be represented by the double equilibrium:

$$CaC_2O_4 \text{ (solid)} \rightleftarrows CaC_2O_4 \text{ (dissolved)} \rightleftarrows Ca^{++} + C_2O_4^{--}.$$

If an acid is added to such a mixture, there will be a tendency for the H^+ ions to combine with $C_2O_4^{--}$ ions to form un-ionized molecules of $H_2C_2O_4$, depending upon the amount of H^+ ions present. Such a reaction will shift the equilibrium to the right, resulting in the solution of the undissolved CaC_2O_4. Now HCl is highly ionized, so that the effect in its case will be very large. On the other hand, $HC_2H_3O_2$ is a very weak acid (much weaker than $H_2C_2O_4$) and does not offer enough H^+ ions to form an appreciable amount of $H_2C_2O_4$ molecules. Consequently, the solvent action of $HC_2H_3O_2$ on CaC_2O_4 is practically nil.

2. *The Flame Test.*—Make the flame test on a little $CaCl_2$ solution.

3. *Formation of Calcium Ferrocyanide.*—Dilute 1 cc. of $CaCl_2$ solution with 3 or 4 volumes of water, and add 1 cc. of NH_4Cl solution and 2 or 3 cc. of $K_4Fe(CN)_6$ solution (?, E). The precipitate is a mixed salt, and its composition may be qualitatively represented by the formula, $CaKNH_4Fe(CN)_6$. (Separation of Ca^{++} from Sr^{++}.)

Exercises

1. By what other names is Group IV known?
2. Is $Ca(OH)_2$ a very soluble substance? Then why was it not precipitated in Group III?
3. What salt of the ions of Group IV is most uniformly insoluble?
4. What makes the separation of Sr^{++} and Ca^{++} in water solution so difficult? Name one reagent which gives a fairly "clean" separation.
5. Can $BaSO_4$ be precipitated from $BaCl_2$ solution by a saturated solution of $SrSO_4$?
6. Suppose saturated solutions of $Sr(NO_3)_2$ and K_2CrO_4 were mixed. Would it be expected that a precipitate of $SrCrO_4$ would form?
7. Can Ca^{++} be tested for by $(NH_4)_2C_2O_4$ solution in the presence of Ba^{++} and Sr^{++}?
8. Why, after the removal of Sr^{++} by $(NH_4)_2SO_4$ solution, is the CaC_2O_4 precipitate always small?
9. What is the requisite condition for the complete precipitation of Ba^{++} by $K_2Cr_2O_7$ solution?
10. Compare the amounts of the following anions that could be present in a solution containing excess of H^+ ions: $C_2O_4^{--}$, $C_2H_3O_2^-$, Cl^-.

11. A Group IV solution gives a precipitate with $(NH_4)_2CO_3$ solution, but none with $CaSO_4$ solution. What ion is indicated?

12. Explain the solubility of $CaCO_3$ in boiling NH_4Cl solution.

ANALYSIS

(64) Precipitation.—To the filtrate from Group III add dilute HCl in slight excess (litmus test), and evaporate the mixture in a Pyrex beaker to a volume of about 25 cc. Filter out any precipitate (sulfur), and wash it with a little water, adding the washings to the main filtrate. Reject the precipitate.

In case of unknowns on Group IV only, omit the evaporation, but add 5 cc. of NH_4Cl solution, and dilute to 25 cc.

Add NH_4OH in slight excess, heat to boiling, remove the flame from beneath the beaker, and add $(NH_4)_2CO_3$ solution until the precipitation appears complete. Stir well, and allow the mixture to stand 15 minutes. If a precipitate forms, filter and wash the precipitate, adding the first washings to the main filtrate. Reserve the precipitate for the last paragraph of this section.

Note.—Alkaline earth carbonates when precipitated in cold solutions are flocculent and hard to filter, but crystalline and readily filterable when precipitated from hot solutions.

Removal of Traces of Group IV Ions.—Divide the solution from the preceding paragraph into two approximately equal portions. To one add 1 cc. of $(NH_4)_2SO_4$ solution, shake, and allow to stand 15 minutes. A slight precipitate[1] (or turbidity) indicates Ba^{++} (or possibly Sr^{++}). To the second portion add 1 cc. of $(NH_4)_2C_2O_4$ solution, shake, and allow to stand 15 minutes. A slight precipitate (or turbidity) indicates Ca^{++} (or Sr^{++}). Recombine the two portions with their precipitates, warm, shake, and filter. Reject the precipitate, and reserve the filtrate for **(75)**.

[1] Very small precipitates in solutions in beakers may sometimes be made easily visible by allowing the precipitate to settle and then giving the solution a whirling motion by gently shaking the beaker. The precipitate will be carried to the center of the whirlpool.

In test tubes the precipitate is best seen by looking upward through the bottom of the tube.

Notes.—1. In the presence of ammonium salts the precipitation of the carbonates of the alkaline earth metals is not complete. This is due in some degree to the existence of equilibria such as $CaCO_3 + 2NH_4Cl \rightleftarrows CaCl_2 + (NH_4)_2CO_3$. There is also evidence that soluble double salts may exist, as $CaCO_3.(NH_4)_2CO_3$.

2. Traces of the Group IV cations are removed in the above procedure to keep them from passing into Group V, where they would interfere with the test for Mg^{++}. The phosphates of Ba^{++}, Sr^{++}, and Ca^{++} are insoluble, and would give precipitates with the Mg reagent, Na_2HPO_4 solution, which might be mistaken for a test for this Group V ion.

Dissolve the $(NH_4)_2CO_3$ precipitate by repeatedly pouring a 5- to 10-cc. portion of hot $HC_2H_3O_2$ through the filter, reheating between extractions. Proceed to (**65**) or (**68**) (Instructions).

Method A

(**65**) **Barium.**—Dilute the acid solution from (**64**) to about 50 cc., add 5 cc. of concentrated $NaC_2H_3O_2$ solution, and heat to boiling. Add $K_2Cr_2O_7$ solution gradually until it is present in slight excess, as evidenced by a yellow filtrate. Boil and filter while hot.[1] Wash the precipitate with a little hot water, and dissolve it by pouring 2 or 3 cc. of concentrated HCl through the filter, receiving the filtrate in a test tube. Wash the paper with a few drops of water, adding the washings to the filtrate. Boil the solution until it is an intense green and all the free Cl_2 has been expelled, and then test it in the flame by means of a clean platinum wire (see (**61**, 3)). A green flame is confirmatory of Ba^{++}.

Notes.—1. The confirmatory flame test for Ba^{++} is necessary only when large amounts of Sr^{++} are present. With high concentrations of Sr^{++}, $K_2Cr_2O_7$ gives a precipitate of $SrCrO_4$, even in the presence of $HC_2H_3O_2$. (See Solubility Table, page 54.)

2. Upon boiling a mixture of $BaCrO_4$ and HCl, the chromate is reduced, $CrCl_3$ being formed. The equation may be written $2BaCrO_4 + 16HCl \rightarrow 2BaCl_2 + 2CrCl_3 + 8H_2O + 3Cl_2$.

3. Flame tests are due to the presence in the flame of some compound of the element in *gaseous* form. For this reason the test is usually made on chlorides, which seem to have the highest relative volatility of all metallic compounds. Compounds of very low volatility, as chromates, phosphates, and silicates, give very weak flame tests.

[1] $BaCrO_4$ is colloidal and hard to filter unless precipitated from hot solutions.

(66) **Strontium.**—To about 5 cc. of the filtrate from (65) in a test tube add 1 or 2 cc. of clear $CaSO_4$ solution. Shake, and if a precipitate does not form, warm and allow to stand 10 minutes. Compare this with the remainder of the solution. If the smaller portion is turbid, a precipitate of $SrSO_4$ is present; if exactly like the larger portion, Sr^{++} is absent. Discard the smaller portion.

If Sr^{++} is present, add to the larger portion $(NH_4)_2SO_4$ solution as long as more precipitate appears to form, warm, shake vigorously, and allow to stand 10 minutes. Filter out any precipitate ($SrSO_4$ and $CaSO_4$), wash, and reserve the filtrate for (67). Reject the precipitate.

If Sr^{++} is absent, omit the $(NH_4)_2SO_4$ treatment, and proceed directly to (67).

(67) **Calcium.**—Set aside a small portion of the solution from (66) for reference. To the remainder add 1 or 2 cc. of $(NH_4)_2C_2O_4$ solution and allow to stand for at least 15 minutes. Now compare the two portions. A turbidity in the second indicates the presence of Ca^{++}.

Notes.—1. The CaC_2O_4 precipitate usually forms promptly and generally in appreciable amounts. In the absence of Ca^{++} and in the presence of Sr^{++}, a slight precipitate of SrC_2O_4 may form, especially upon standing. This may be distinguished from the real CaC_2O_4 precipitate by a control experiment as follows: Add to some $SrSO_4$ solution (side shelf) a drop or two of $K_2Cr_2O_7$ (to give the yellow color), and then some $(NH_4)_2C_2O_4$ solution. If the precipitate in the unknown solution is larger than in the control, Ca^{++} is present.

2. The Sr^{++} and Ca^{++} are sometimes separated from the $K_2Cr_2O_7$ solution by precipitation with $(NH_4)_2CO_3$. After the soluble chromate has been washed out, the $SrCO_3$ and $CaCO_3$ are redissolved in $HC_2H_3O_2$. Such a procedure is not necessary chemically, but is used because many students profess to have difficulty in seeing precipitates in yellow or orange solutions. This trouble is completely obviated by the use of the control tests described above.

TABLE XI.—ANALYSIS OF GROUP IV
(Method A)

(64) Solution containing Ba^{++}, Sr^{++}, Ca^{++}, and possibly members of Group V. If filtrate from Group III, add HCl, evaporate to 25 cc.; if Group IV only, add 5 cc. NH_4Cl solution and dilute to 25 cc. Add NH_4OH, heat to boiling, add $(NH_4)_2CO_3$. Filter, wash precipitate.

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolve in hot $HC_2H_3O_2$. (65) Dilute to 50 cc., add $NaC_2H_3O_2$ solution, and $K_2Cr_2O_7$ solution in slight excess. Boil, filter hot, wash precipitate.

Filtrate: Traces of Ba^{++}, Sr^{++}, Ca^{++}, also Group V. Add $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, filter. Filtrate: Group V. (See Table XIII)

Precipitate: Yellow $BaCrO_4$. Dissolve in HCl, boil out Cl_2, make flame test. Green flame indicates Ba^{++}.

(66) Filtrate: Sr^{++}, Ca^{++}, $Cr_2O_7^{--}$. To 5 cc. of solution add $CaSO_4$ solution, warm, and let stand 10 minutes. Precipitate: $SrSO_4$. Discard solution and precipitate.

If Sr^{++} is absent, test larger portion for Ca^{++} by (67); if Sr^{++} is present, add to larger portion $(NH_4)_2SO_4$ in slight excess. Warm, filter, wash precipitate.

Precipitate: White $SrSO_4$, $CaSO_4$. Discard.

(67) Filtrate: Sat. $CaSO_4$ solution, containing $K_2Cr_2O_7$. Divide, add $(NH_4)_2C_2O_4$ to larger portion and compare with smaller portion. Precipitate: White CaC_2O_4.

METHOD B

(68) **Barium.**—To a small sample of the solution from (64) add an equal volume of $NaC_2H_3O_2$ solution and a few drops of $K_2Cr_2O_7$ solution. A yellow precipitate,[1] $BaCrO_4$, indicates the presence of Ba^{++}. Reject the mixture.

If Ba^{++}, is absent, treat the remainder of the solution from (64) by (69); if Ba^{++} is present, proceed as follows:

Dilute the remainder of the solution to about 50 cc. and add 5 cc. of $NaC_2H_3O_2$ solution. Heat to boiling and add $K_2Cr_2O_7$

[1] If in doubt as to the presence or absence of a precipitate, add the $NaC_2H_3O_2$ and $K_2Cr_2O_7$ reagents to a little distilled water, and compare this blank test with the actual test.

solution in slight excess; *i.e.*, until the filtrate is yellow. Boil and filter while hot.[1] Reserve the filtrate for (**69**). Wash the residue and dissolve it in 2 or 3 cc. of concentrated HCl. Boil the solution until it is an intense green and the free Cl_2 has been expelled, and then test it in the flame with a clean platinum wire. A green flame is confirmatory for Ba^{++}.

Note.—The confirmatory test for Ba^{++} is necessary only when large amounts of Sr^{++} are present. With high concentrations of Sr^{++}, $K_2Cr_2O_7$ gives a precipitate of $SrCrO_4$, even in the presence of $HC_2H_3O_2$. (See Solubility Table, page 54.)

(**69**) **Calcium.**—If Ba^{++} was found in (**68**), proceed according to *A*; if Ba^{++} was absent, proceed according to *B*.

A. To the solution from (**68**), containing the excess of $K_2Cr_2O_7$, add NH_4OH to alkalinity (litmus test), heat to boiling, withdraw the flame from beneath the beaker, and add $(NH_4)_2CO_3$ in slight excess. A precipitate[2] indicates the presence of Ca^{++} or Sr^{++}, or both. Allow the mixture to stand 15 minutes, filter, and wash until the precipitate is white and the fresh washings are colorless. Dissolve the precipitate in a small amount of $HC_2H_3O_2$, and evaporate to a volume of 5 cc. If a precipitate forms, dissolve it in the minimum amount of water. Proceed to the last paragraph of *B* of this section.

B. Treat the main portion of the solution from (**68**) as follows: Add 10 cc. of NH_4Cl solution, and then $K_4Fe(CN)_6$ solution in slight excess (indicated by a yellow filtrate). Do not heat, since acidified solutions of ferrocyanides, upon warming, form a precipitate of ferrous cyanide, $Fe(CN)_2$. A white precipitate, $CaKNH_4Fe(CN)_6$, forming at once, indicates the presence of Ca^{++}. Filter, and proceed to (**70**).

Note.—The excess of $K_2Cr_2O_7$ is removed, since it interferes with the $K_4Fe(CN)_6$ reaction. It is more convenient to make the separation by reprecipitating the Ca^{++} and the Sr^{++} as carbonates than by reducing the $Cr_2O_7^{--}$ to Cr^{+++} and precipitating the latter as $Cr(OH)_3$.

[1] $BaCrO_4$ is colloidal and hard to filter unless precipitated from hot solutions.

[2] The presence of a precipitate may be known by comparing the mixture with some dilute $(NH_4)_2CO_3$ to which a few drops of $K_2Cr_2O_7$ solution have been added. A turbidity in the former indicates precipitate formation.

(70) Strontium.—Set aside a small portion of the filtrate from (**69**) for reference. To the larger portion add a few drops of $(NH_4)_2SO_4$ solution, shake well, and let stand for 15 minutes. Compare with the smaller portion. A white precipitate of $SrSO_4$ in the larger portion, sometimes forming slowly, indicates Sr^{++}.

TABLE XII.—ANALYSIS OF GROUP IV
(METHOD B)

(**64**) Solution containing Ba^{++}, Ca^{++}, and Sr^{++}, and possibly members of Group V. If filtrate from Group III, add HCl, evaporate to 25 cc.; if Group IV only, add 5 cc. NH_4Cl and dilute to 25 cc. Add NH_4OH, heat to boiling, add $(NH_4)_2CO_3$. Filter, wash residue.

Precipitate: $BaCO_3$, $CaCO_3$, $SrCO_3$. Dissolve in hot $HC_2H_3O_2$. (**68**) To a small sample of the solution add $K_2Cr_2O_7$ solution. Yellow precipitate, $BaCrO_4$, indicates Ba^{++}. If Ba^{++} is absent, proceed to (**69**); if present, dilute to 50 cc., add $NaC_2H_3O_2$ solution, and $K_2Cr_2O_7$ solution in small excess. Heat to boiling, filter, wash precipitate.		Filtrate: Traces of Ba^{++}, Ca^{++}, Sr^{++}; also Group V. Add $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, filter. Filtrate: Group V. (See Table XIII)
Precipitate: Yellow $BaCrO_4$. Dissolve in HCl, boil out Cl_2, make flame test. Green flame indicates Ba^{++}.	(**69**) Filtrate: Ca^{++}, Sr^{++}; also $Cr_2O_7^{--}$, if Ba^{++} was present. If Ba^{++} was present, proceed to *A*; if Ba^{++} was absent, proceed to *B*. *A*. Add NH_4OH, $(NH_4)_2CO_3$, filter, wash precipitate.	
	Filtrate: $K_2Cr_2O_7$. Reject. / Precipitate: $CaCO_3$, $SrCO_3$. Dissolve in $HC_2H_3O_2$, and concentrate. Proceed to *B*.	
	B. Add NH_4Cl and excess $K_4Fe(CN)_6$ solution, and filter.	
	Precipitate: White $CaK_2Fe(CN)_6$. / Filtrate: Sr^{++}, excess $K_4Fe(CN)_6$. (**70**) Divide, saving smaller portion for reference. To larger portion add $(NH_4)_2SO_4$. Precipitate: White $SrSO_4$.	

GROUP V. THE SOLUBLE GROUP

This group contains Mg^{++}, Na^{+}, K^{+}, and NH_4^{+}. No single anion forms salts with these ions sufficiently insoluble for the group to be precipitated as a whole; consequently, this group is said to have no group reagent.

The group is called "The Soluble Group," because its salts are characterized by marked solubility, particularly in water containing ammonium salts. On account of the presence of the ions of the alkali metals, potassium and sodium, the group is sometimes called "The Alkali Group." In view of the presence of magnesium, which is quite different in its chemical nature from the alkali metals, this name seems hardly as appropriate as the former one.

In the absence of ammonium salts, Mg^{++} forms several compounds (*e.g.*, $Mg(OH)_2$) of sufficiently low solubility to admit of a "clean" separation from the other members of the group. But fairly high concentrations of ammonium salts are normally present, having been introduced in the precipitation of Groups III and IV. In this case, advantage is taken of the comparatively low solubility of magnesium ammonium phosphate, $MgNH_4PO_4$, to effect a separation from the other ions of the group.

PRELIMINARY EXPERIMENTS

(71) Magnesium, Mg^{++}. 1. *Solubility of Magnesium Hydroxide in Ammonium Salt Solutions.*—Dilute 2 cc. of magnesium nitrate solution, $Mg(NO_3)_2$, to about 6 cc., and divide into two parts. To the first portion add NH_4OH drop by drop (E). To the second add an equal volume of NH_4Cl solution, and then NH_4OH (?).

This solvent action of NH_4^{+} salts on $Mg(OH)_2$ prevents its precipitation in what previous group?

2. *Solubility of Magnesium Carbonate in Ammonium Salt Solutions.*—Dilute 2 cc. of $Mg(NO_3)_2$ solution and divide as in the preceding experiment. To the first part add Na_2CO_3 (E). To the second add NH_4Cl solution and then Na_2CO_3 solution (?).

In what previous group was the precipitation of $MgCO_3$ prevented by the presence of NH_4^{+} compounds?

3. *Precipitation of Magnesium Ammonium Phosphate.*—To a dilute solution of $Mg(NO_3)_2$ add NH_4OH[1] to alkaline reaction, NH_4Cl solution until any precipitate of $Mg(OH)_2$ is dissolved, and then a little Na_2HPO_4 solution (E). (SEPARATION OF Mg^{++} FROM K^+, Na^+.) The precipitate is $MgNH_4PO_4$. Note its appearance closely.

Notes.—1. The NH_4Cl does not appear in the equation for the formation of $MgNH_4PO_4$. Its purpose is merely to prevent the formation of $Mg(OH)_2$.

2. $MgNH_4PO_4$ is readily hydrolyzed into gelatinous $MgHPO_4$, and for that reason it is precipitated from concentrated, rather than dilute, solutions. Since $MgNH_4PO_4$ is much more insoluble than $MgHPO_4$, the test is furthermore much more sensitive when made in concentrated solutions.

4. *Distinction from Sodium and Potassium.*—Magnesium salts give no coloration to the Bunsen flame, and form no precipitates with perchloric acid, $HClO_4$, and fluosilicic acid,[2] H_2SiF_6, solutions.

(**72**) **Sodium, Na^+.** 1. *Flame Test.*—Clean a platinum wire by repeatedly dipping it in some HCl solution in a test tube and heating it in the non-luminous Bunsen flame until practically no color appears. Now dip it into dilute NaCl solution and try the flame color (?). Clean the wire again, draw through the fingers, and try the flame color (?). Compare the duration and intensity in the two cases (?).

2. *Precipitation of Sodium Fluosilicate.*—Dilute 2 cc. of NaCl solution with an equal volume of water, add 4 cc. of ethyl alcohol, C_2H_5OH (storeroom), and a few drops of fluosilicic acid solution, H_2SiF_6 (storeroom) (E).

(**73**) **Potassium, K^+.** 1. *Flame Test.*—Clean a platinum wire as in (**72**, 1) and try the flame test with KCl solution (?).

To the KCl solution add 1 drop of NaCl solution, and then repeat the flame test (?). Now observe the color of the flame through a thick cobalt glass (?).

Note.—The purple or violet color of the potassium flame is a mixture of red and blue, both of which are transmitted by cobalt glass, while the

[1] The NH_4OH and Na_2HPO_4 solutions should be filtered if they are not perfectly clear.

[2] Formerly called "hydrofluosilicic" acid. The shorter name is in accord with the conventional system for naming substituted oxygen acids, and should displace the "hydro" form.

yellow of the sodium flame is not. The contrast with the blue background of the cobalt glass brings out the red of the potassium flame quite sharply.

2. *Precipitation of Potassium Perchlorate.*—Dilute 1 cc. of KCl solution to about 4 cc., add 4 cc. of ethyl alcohol, C_2H_5OH (storeroom), and a few drops of perchloric acid solution, $HClO_4$ (storeroom) (E). Shake and note the crystalline nature of the precipitate. (SEPARATION OF K^+ FROM Na^+.)

3. *Formation of Potassium Fluosilicate.*—Dilute 1 cc. of KCl solution with 3 cc. of water, add 4 cc. of alcohol (storeroom) and a few drops of fluosilicic acid, H_2SiF_6 (storeroom) (E). Is this precipitate crystalline or colloidal?

(74) Ammonium, NH_4^+. 1. *Action of Strong Bases on Ammonium Salts.*—Warm a little NH_4Cl solution in a beaker with NaOH solution (E). By means of a few drops of water stick a piece of red litmus paper to the lower side of a watch glass and place it over the beaker. Warm gently, and note the effect (?).

Repeat the experiment, using NaOH solution without the NH_4Cl, but boiling.

Note.—Several facts combine to account for the displacement of free NH_3 from ammonium salts by strong bases. The series of equilibria involved may be represented as follows:

$$\left.\begin{matrix} NH_4Cl \\ + \\ NaOH \end{matrix}\right\} \underset{(1)}{\rightleftharpoons} \left\{\begin{matrix} NH_4OH \\ + \\ NaCl \end{matrix}\right. \overset{(2)}{\rightleftharpoons} \left\{\begin{matrix} NH_3\ (\text{dissolved}) \\ + \\ H_2O \end{matrix}\right. \overset{(3)}{\rightleftharpoons} NH_3(\text{gas}).$$

In the first place, NH_4OH is a very weak base, a molar solution being ionized only 0.4 per cent; hence, reaction (1) proceeds almost to completion. In the second place, NH_4OH is largely dissociated into NH_3 and H_2O, as represented in reaction (2). This dissociation operates to remove the NH_4OH to a large degree, thereby displacing the equilibrium in (1) still further to the right. In the third place, NH_3 is a gas, and its solubility in water becomes quite low at high temperatures, according to reaction (3). At high temperatures, then, reaction (3) is practically complete, and hence reactions (2) and (1) will, in turn, be made to go to practical completion. Note, however, that the removal of the NH_3 depends wholly on reaction (3). Reactions (1) and (2) merely operate to convert NH_4^+ with practical completeness into dissolved NH_3.

2. *Reaction with Fluosilicic Acid.*—To 2 or 3 cc. of NH_4OH solution add an equal volume of alcohol (storeroom) and a few drops of H_2SiF_6 solution (storeroom) (?). The gelatinous precipitate appears to be $Si(OH)_4$, formed by the decomposition of H_2SiF_6, thus: $6NH_4OH + H_2SiF_6 \rightarrow Si(OH)_4 + 6NH_4F + 2H_2O$. Note that $Si(OH)_4$ resembles Na_2SiF_6 closely in appearance. (See (**72, 2**).)

Note.—Ammonium salts usually give no precipitate with H_2SiF_6. However, if they are present in considerable amount, and particularly if the solution contains no acid, the above decomposition is apt to occur. Hence, it is the safer policy to remove ammonium salts by ignition before testing for Na^+ by the H_2SiF_6 reagent.

3. *Removal of Ammonium Salts.*—Place 2 cc. of NH_4Cl solution in a Pyrex beaker, evaporate to dryness, and carefully heat the residue just below red heat[1] (?). Does the salt tend to condense (*i.e.*, sublime) on the sides of the beaker?

Repeat the experiment, only adding 3 or 4 cc. of concentrated HNO_3 before evaporating, and moistening the residue with 2 or 3 drops of concentrated HNO_3 just before ignition. Does a sublimate form in this case?

Which appears to be the better method for expelling ammonium salts?

Notes.—Upon heating, NH_4Cl partially dissociates according to the equation, NH_4Cl + heat $\rightleftarrows NH_3 + HCl$. As inferred from the Le Chatelier principle, the degree of dissociation is much greater at high temperatures. As a result, a sublimate of solid NH_4Cl tends to form whenever hot vapors come in contact with a relatively colder surface, and falls back to the bottom of the beaker to enter again upon a cycle of vaporization and sublimation.

2. Upon strong heating, NH_4NO_3 decomposes into water and nitrous oxide, thus: $NH_4NO_3 \rightarrow 2H_2O + N_2O$. Strictly speaking, decomposition differs from dissociation in that the former is irreversible.

Exercises

1. The solubility of $MgNH_4PO_4$ is 0.064 millimoles per liter. Compare with $Mg(OH)_2$. Why would not NaOH be a suitable reagent for the precipitation of Mg^{++}?
2. Given the equilibrium, $Mg(OH)_2$ (solid) $\rightleftarrows Mg(OH)_2$ (dissolved) $\rightleftarrows Mg^{++} + 2OH^-$. How would this equilibrium be affected by the addition of an ammonium salt?

[1] This ignition may be very conveniently carried out by placing the beaker on a wire gauze with an asbestos pad, and heating with the full strength of the Bunsen flame.

3. NH_4Cl prevents the precipitation of $Mg(OH)_2$ by NH_4OH. Would NaCl also prevent the precipitation of $Mg(OH)_2$ by NaOH? Why?
4. Write the equation for the hydrolysis of $MgNH_4PO_4$, forming $MgHPO_4$. How may this hydrolysis be prevented?
5. What is the color of the potassium flame as seen through a cobalt glass? Explain.
6. Why not use H_2SO_4 in cleaning a platinum wire, instead of HCl, as in (**72**, 1)?
7. Can Na^+ be tested for in the presence of K^+ by means of H_2SiF_6 solution? Why?
8. Why are K^+ and Na^+ precipitated in 50 per cent alcohol solution? As a rule, are inorganic salts as soluble in alcohol as in water?
9. Why should the reaction between $HClO_4$ and C_2H_5OH be expected to be violently explosive?
10. Just how would NH_4^+ interfere with the tests for Na^+ and K^+ if not previously removed?
11. Why will NH_4OH give a precipitate with H_2SiF_6 solution, while NH_4Cl of the same concentration will not?
12. Why is the test for NH_4^+ always made on a portion of the original solution?
13. What is the difference between decomposition and dissociation? Illustrate by the effect of heat upon dry NH_4Cl and dry NH_4NO_3.
14. How could Mg^{++} be separated from Na^+ and K^+ without the introduction of Na^+ ions?
15. A solution containing only Group V ions gives a white precipitate with NaOH solution, but the vapors do not turn red litmus paper blue. Interpret.
16. Name suitable reagents for the following one-step separations: (*a*) $Mg(NO_3)_2$ and KNO_3; (*b*) $MgCl_2$ and NaCl; (*c*) KNO_3 and $NaNO_3$; (*d*) $NaNO_3$ and NH_4NO_3.

ANALYSIS

(**75**) **Magnesium.**—Place about one-third of the solution from (**64**) (or unknown on Group V) in a test tube, reserving the remainder for subsequent procedures. By means of a filter paper in a funnel, carefully filter in concentrated NH_4OH (side shelf) until the solution is distinctly alkaline. If a precipitate forms, try to dissolve it by filtering into the solution through the same paper NH_4Cl solution (not more than 3 or 4 cc.). If an insoluble residue remains, warm and shake to coagulate the precipitate. Filter and discard the residue. Filter into the clear filtrate 1 or 2 cc. of Na_2HPO_4 solution and shake well. A white crystalline precipitate, $MgNH_4PO_4$, indicates Mg^{++}. Sometimes a very per-

sistent case of supersaturation is met at this point, which may be broken down by gently rubbing the inside of the tube with the fire-polished end of a stirring rod, or by allowing the tube to stand for several hours.

Notes.—1. Certain reagents like concentrated NH_4OH and Na_2HPO_4 tend to become "dreggy" upon standing, owing to reactions with the glass of the reagent bottles. These dregs must be filtered out, else the formation of the $MgNH_4PO_4$ precipitate may be obscured.

2. Upon adding NH_4OH to the acid solution, Mg^{++} may be precipitated as $Mg(OH)_2$, soluble in NH_4Cl solution.

3. The residue insoluble in NH_4Cl solution may be H_2SiO_3, or some compound of an ion of a previous group not completely precipitated in its turn. Small amounts of $Al(OH)_3$ or CaC_2O_4 may appear at this point. All these materials are insoluble in NH_4Cl solution, and are thereby eliminated.

(**76**) **Ammonium.**—Put a small sample of the *original* substance (solid or solution) in a small beaker, add excess of NaOH solution, and warm. (*Do not boil.*) Cover the beaker with a watch glass, to the lower side of which has been attached a piece of moist red litmus paper. If the litmus paper turns blue, the presence of NH_3 fumes is indicated, showing the presence of NH_4^+ compounds in the unknown.

Notes.—1. Since ammonium compounds have been introduced into the solution as reagents in Groups III and IV, the test for NH_4^+ must be made on a fresh sample of the unknown.

2. If the mixture is allowed to boil, enough NaOH may be carried up in the spray to give a blue color to the litmus paper.

(**77**) **Potassium.**—If the solution reserved from (**75**) is a filtrate from a Group IV analysis, or if NH_4^+ was found in (**76**), proceed according to *A*. On the other hand, if the solution is an unknown containing Group V only, and if NH_4^+ has been shown to be absent by (**76**), proceed directly to *B*.

A. Add to the solution 5 cc. of concentrated HNO_3 and evaporate to dryness in a small Pyrex beaker. Cool, moisten the residue with a few drops of concentrated HNO_3, and ignite the residue by heating the beaker strongly on a wire gauze, so as to decompose the NH_4NO_3 formed. Cool, add about 5 cc. of water and a few drops of dilute HCl, and filter out any insoluble residue. Wash the residue with 1 cc. of water, adding the washings to the main filtrate.

Note.—A black residue may appear upon evaporating the solution to dryness. This is due to organic matter introduced in the NH_4OH (pyridine bases) or perhaps extracted from the filter paper, and is completely burned out during the ignition of the dry residue.

B. Make a flame test on the solution, using a clean platinum wire. A violet color indicates K^+, and a yellow color Na^+. If Na^+ is present, observe the flame color through a thick or double cobalt glass. A purplish color as seen through the cobalt glass indicates K^+.

Transfer the solution to a test tube, cool thoroughly, and add an equal volume of ethyl alcohol, C_2H_5OH (storeroom). If a precipitate forms, filter and discard the residue. Add perchloric acid, $HClO_4$ (storeroom), in slight excess. Shake well and let stand for a few minutes. A white crystalline precipitate is $KClO_4$, showing the presence of K^+. Filter, and add a few drops of $HClO_4$ to the filtrate, to test for the completeness of the $KClO_4$ precipitation. Filter out any precipitate and reserve the solution for (**78**).

Note.—The solution must not be heated after the addition of the $HClO_4$. Upon heating, alcohol and perchloric acid may react with explosive violence. Furthermore, $KClO_4$ becomes appreciably soluble upon warming.

(**78**) **Sodium.**—To the solution from (**77**) add H_2SiF_6 (storeroom). A white gelatinous precipitate of Na_2SiF_6 indicates Na^+.

Note.—If the $HClO_4$ precipitation of the K^+ was not complete, a gelatinous precipitate of K_2SiF_6 may form at this point.

TABLE XIII.—ANALYSIS OF GROUP V

(**75**) Solution: Mg^+, NH_4^+, K^+, Na^+. Divide, reserving larger portion. To smaller portion add concentrated NH_4OH, NH_4Cl solution to redissolve any precipitate, and Na_2HPO_4 solution. Precipitate: White crystalline $MgNH_4PO_4$.

(**76**) To a small portion of the *original substance* in a small beaker add excess of NaOH solution, and warm. Vapors turning red litmus blue indicate NH_4^+.

(**77**) Solution: Larger portion from (**75**). If NH_4^+ may be present, proceed according to *A*; if NH_4^+ is known to be absent, proceed according to *B*.

A. Add 5 cc. of concentrated HNO_3 and evaporate to dryness. Moisten the residue with concentrated HNO_3 and ignite. Cool, take up residue in 5 cc. of water and a little HCl, filter, wash the precipitate with a few drops of water. Reject the residue. Solution: Mg^{++}, K^+, Na^+. Proceed to *B*.

B. Make flame test on the solution, with and without cobalt glass. Violet color, or purple color through cobalt glass, indicates K^+; yellow color, Na^+. Add equal volume of alcohol and excess of $HClO_4$. Shake, filter, wash precipitate with a few drops of cold water.

Precipitate: White $KClO_4$.	(**78**) Filtrate: Na^+, (Mg^{++}), alcohol. Add H_2SiF_6 and shake. Precipitate: White, gelatinous Na_2SiF_6.

PART II

DETECTION OF THE IONS OF THE NON-METALS

The non-metals sometimes occur free, but they are more frequently found in combination, usually in negative radicals. Carbon, for example, occurs free in cast iron as graphite, and combined in limestone, $CaCO_3$, in the negative carbonate group. Analytical procedure usually involves the conversion of free elements into the form of ions, and, in such cases, the detection of these ions is taken as evidence of the presence of the free elements.

Anion analysis was formerly referred to as "acid analysis," since the anions are the distinctive radicals of acids. However, since it is almost always the anion, and not the acid, which is detected, and since the acids can occur as such only in acid solutions, the term "anion analysis" seems much preferable.

Anion analysis differs from cation analysis in one respect, *viz.:* In the detection of the metallic ions, with only a few exceptions, the ion must be isolated from other cations before the specific test is applied; on the other hand, the anion tests may be made, for the most part, in the presence of other anions, and therefore may usually be made on the original substance. There are some cases, however, in which one ion does interfere with the test for another anion, and then separations are necessary.

Anion Groups.—It is easily seen that if anions were divided into groups which could be tested for by group reagents, the analytical procedure might be considerably shortened by testing for only those anions whose groups were found to be present. It would be a very unusual case to find members of all the anion groups present in one unknown.

The reagents used in determining the anion groups present in an unknown substance are silver nitrate solution, $AgNO_3$,

and barium nitrate solution, $Ba(NO_3)_2$. Upon the basis of their reactions with these reagents, the following anion groups are recognized:

Group I.—Anions whose Ag salts are insoluble in water and in dilute HNO_3, and whose Ba salts are soluble in water: *chloride, bromide, iodide, cyanide, thiocyanate, ferrocyanide, ferricyanide, sulfide.*

Group II.—Anions whose Ag salts are slightly soluble in water, but easily soluble in dilute HNO_3; and whose Ba salts are soluble in water: *nitrite, acetate, hydroxide.*

Group III.—Anions whose Ag salts are insoluble in water, but soluble in dilute HNO_3; and whose Ba salts are insoluble in water, but soluble in dilute HNO_3. This group is divided into two subgroups on the basis of the color of the Ag salt:

(*a*) Anions whose Ag salts are white: *sulfite, carbonate, oxalate, borate, tartrate.*

(*b*) Anions whose Ag salts are colored: *phosphate* (yellow), *arsenate* (brown), *arsenite* (yellow), *thiosulfate* (brown-black[1]), *chromate* (dark red).

Group IV.—Anions whose Ag and Ba salts are soluble in water: *nitrate, chlorate, permanganate.* Since $AgNO_2$ and $AgC_2H_3O_2$ are somewhat soluble, *nitrite* and *acetate* might be included.

Group V.—Anions whose Ag salts are soluble in water, but whose Ba salts are insoluble in both water and dilute HNO_3: *sulfate, fluoride.*

Group VI.—Anions which, upon acidification and evaporation, leave an insoluble residue: *silicate.* All the silicates are insoluble except Na_2SiO_3 and K_2SiO_3.

Group VII.—Organic Anions whose compounds char upon heating or upon acidification with concentrated H_2SO_4. Among the commoner members of this group are tartrate, citrate, benzoate, salicylate, and many others. Since they belong more particularly to the realm of organic chemistry, they are not included in these procedures.

The relationship between Anion Groups I to V is shown in tabular form in Table XIV.

[1] Silver thiosulfate, $Ag_2S_2O_3$, is really white, but very rapidly undergoes hydrolysis, giving black Ag_2S: $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$.

TABLE XIV.—DETERMINATION OF ANION GROUPS

		Reaction with $AgNO_3$			
		No effect	White precipitate soluble in HNO_3	Colored precipitate soluble in HNO_3	Precipitate insoluble in HNO_3
Reaction with $Ba(NO_3)_2$	No effect	IV	II		I
	Precipitate soluble in HNO_3		III(*a*)	III(*b*)	
	Precipitate insoluble HNO_3	V			

GROUP I

This group contains those anions whose Ag^+ salts are insoluble in water and in dilute HNO_3, but whose Ba^{++} salts are soluble in water: Cl^-, Br^-, I^-, CN^-, SCN^-, $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, and S^{--}.

The reactions with concentrated H_2SO_4 and with $AgNO_3$ solution in the presence of HNO_3 are particularly helpful in identifying these ions.

There are numerous interferences in this group. Consequently, the unknowns issued must contain only simple combinations of these ions. Advanced manuals on qualitative analysis may be consulted with reference to these complications.

PRELIMINARY EXPERIMENTS

(79) Chloride, Cl^-. 1. *Reaction with Concentrated Sulfuric Acid.*—Place a little solid NaCl in a test tube, moisten with a drop of water, and add concentrated H_2SO_4 (E). Test for the presence of free chlorine by holding moistened red litmus paper in the fumes (?).

Note.—HCl differs from HBr and HI in not being oxidized by concentrated H_2SO_4.

2. *Precipitation of Silver Chloride.*—Prepare a little AgCl by the action of some chloride solution (*e.g.*, NaCl) with $AgNO_3$ solution. Shake, and become familiar with the color and general appearance of the precipitate. Save for (**81**, 2).

3. *Formation of Chromyl Chloride and Its Hydrolysis.*—Mix one part of dry NaCl with two parts of dry $K_2Cr_2O_7$ in a mortar, grind to a powder, and place a small amount in a 50-cc. distilling flask (storeroom). Cover with concentrated H_2SO_4, add a piece of porous tile (to prevent bumping), cork, and distil as long as brown fumes come over. Receive the distillate in a test tube containing 1 or 2 cc. of water and placed over the delivery tube of the flask, as shown in Fig. 8. *The delivery tube should not dip under the water. Water might be drawn back into the flask, and a dangerous explosion would occur.* What is the color of the solution in the tube? Add an equal volume of sodium acetate solution, $NaC_2H_3O_2$, and a few drops of barium chloride solution, $BaCl_2$. The yellow precipitate is $BaCrO_4$.

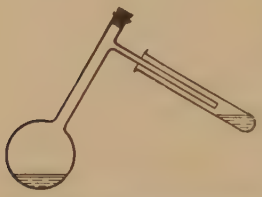

FIG. 8.—Distillation of chromyl chloride.

Note.—A mixture of chlorides, $K_2Cr_2O_7$, and concentrated H_2SO_4 gives on distillation liquid chromyl chloride, CrO_2Cl_2, boiling at 116°, thus: $4HCl + K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2KHSO_4 + 3H_2O$. The CrO_2Cl_2 is hydrolyzed by the water in the test tube, forming chromic and hydrochloric acids: $CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl$. The chromic acid in the presence of $NaC_2H_3O_2$ gives with Ba^{++} a yellow precipitate of $BaCrO_4$. It thus follows that, while $BaCrO_4$ contains no chlorine, its formation is a test for the presence of Cl^- in the original substance, since it could not form except for the intermediate formation of chromyl chloride. *Cf.* the formation of Hg_2Cl_2 as a test for the presence of Sn, (**23**, 3).

(**80**) **Bromide, Br^-.** 1. *Reaction with Concentrated Sulfuric Acid.*—Place a little solid KBr in a test tube, moisten with a drop of water, and add concentrated H_2SO_4. What is the primary reaction between KBr and H_2SO_4 (E)? What are the colored fumes? Write an equation showing how they are formed from a product of the primary reaction and the excess H_2SO_4 (E).

2. *Silver Bromide.*—Prepare a little AgBr by the action of a bromide solution (*e.g.*, KBr) with dilute $AgNO_3$. Shake and

note closely its color[1] and general appearance. Save for (**81**, 2).

3. *Displacement of Bromine by Chlorine.*—Dilute 1 cc. of potassium bromide solution, KBr, to about 4 cc. and add Cl_2 solution. Explain change in color by means of a labeled equation (E). Add 1 cc. of carbon disulfide, CS_2, and shake vigorously. What is the color of the CS_2 layer? Is this color due to the bromine molecule, Br_2, or to the bromide ion, Br^-?

(**81**) **Iodide, I^-.** 1. *Reaction with Concentrated Sulfuric Acid.*—Place a crystal of potassium iodide, KI (storeroom), in a test tube, moisten with a drop of water, and add concentrated H_2SO_4. Write equation for a primary action similar to the equation for chloride with H_2SO_4, labeling the products with their colors (E). Now explain the colored fumes by a typical equation (E).

2. *Silver Iodide.*—Prepare a little AgI, using dilute KI and $AgNO_3$ solutions. Shake and note closely its color and general appearance. Compare the colors of AgCl, AgBr, and AgI (?).

3. *Oxidation of Iodide Ion by Nitrous Acid.*—Acidify a little KI solution with dilute H_2SO_4 and add KNO_2 solution. Account for the color of the mixture (?, E). Reserve solution for the next test.

Note.—In acid solutions, iodides are oxidized to free iodine by nitrites. A complete equation is: $KI + KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + I_2 + NO + H_2O$. Strictly speaking, the action is between the free acids, thus: $HI + HNO_2 \rightarrow I_2 + NO + H_2O$. Neither HBr nor HCl is oxidized by HNO_2. This is a very important reaction, for it is used not only for separating iodide from bromide and chloride, but also in testing for iodide.

4. *Color of a Carbon Disulfide Solution of Iodine.*—Add 1 cc. of CS_2 to the solution from the preceding experiment and shake. What is the color of the CS_2 layer?

*(**82**) **Cyanide, CN^-.**[2] 1. *Reaction with Acids.*—Cyanides react with acids, forming hydrocyanic ("Prussic") acid, HCN, a deadly poisonous gas.

2. *Formation of Ferrocyanide, $Fe(CN)_6^{----}$, and Prussian Blue.*—To a little potassium cyanide solution, KCN (sodium

[1] Yellow and white cannot be distinguished by artificial (yellow) light.

[2] Cyanides are very violent poisons, and experiments with them should be done only under the oversight of an instructor. It is suggested that cyanides be omitted from most elementary courses.

cyanide, NaCN, may be used), add ferrous sulfate solution, $FeSO_4$, and then NaOH solution to alkalinity. Boil, acidify with dilute HCl. A slight blue precipitate will probably form, owing to the fact that $FeSO_4$ usually contains some Fe^{+++}. Add a few drops of ferric sulfate solution, $Fe_2(SO_4)_3$. The blue precipitate is ferric ferrocyanide, $Fe_4(Fe(CN)_6)_3$ and is called "Prussian blue." The following equations summarize the action:

$$6KCN + FeSO_4 \rightarrow K_4Fe(CN)_6 + K_2SO_4; \text{ and}$$
$$2Fe_2(SO_4)_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4(Fe(CN)_6)_3 + 6K_2SO_4.$$

*(**83**) **Thiocyanate, SCN^-.** 1. *Reaction with Concentrated Sulfuric Acid.*—Thiocyanates are violently decomposed by concentrated H_2SO_4 with the evolution of foul-smelling vapors (carbon oxysulfide, formic acid, sulfur dioxide, etc.) and the deposition of sulfur.

2. *Ferric Thiocyanate.*—Recall the formation of $Fe(SCN)_3$ as a test for Fe^{+++} (E). (See (**46**, 4) and note.)

Note.—Certain organic anions, like acetate, give a red color with Fe^{+++} in neutral solutions, but, unlike thiocyanate, the color disappears on acidifying with HCl.

*(**84**) **Ferrocyanide, $Fe(CN)_6^{----}$.** 1. *Reaction with Concentrated Sulfuric Acid.*—Ferrocyanides are decomposed by hot concentrated H_2SO_4 with the evolution of carbon monoxide, CO (E).

Note.—The equation is $K_4Fe(CN)_6 + 11H_2SO_4 + 6H_2O \rightarrow FeSO_4 + 4KHSO_4 + 6NH_4HSO_4 + 6CO$.

2. *Prussian Blue.*—Ferrocyanide ions combine with Fe^{+++} in acid solution to form Prussian blue, $Fe_4(Fe(CN)_6)_3$, insoluble in excess HCl. (See (**82**, 2).)

*(**85**) **Ferricyanide, $Fe(CN)_6^{---}$.** 1. *Reaction with Concentrated Sulfuric Acid.*—Ferricyanides, like ferrocyanides, are decomposed by hot concentrated H_2SO_4 with the evolution of carbon monoxide, CO (E).

Note.—The equation is $2K_3Fe(CN)_6 + 21H_2SO_4 + 6H_2O \rightarrow Fe_2(SO_4)_3 + 6KHSO_4 + 12NH_4HSO_4 + 12CO$.

(**86**) **Sulfide, S^{--}.** 1. *Reaction with Concentrated Sulfuric Acid.*—Place 2 or 3 drops of sodium sulfide solution, Na_2S, in a test tube and add concentrated H_2SO_4. Carefully smell the gases given off and try to identify, by their odor, two substances present

in the fumes (?). What is the primary reaction between Na_2S and H_2SO_4 (E)? Explain by a second equation the formation of S and SO_2 (E).

2. *Silver Sulfide.*—Dilute 1 or 2 cc. of $AgNO_3$ solution in an Erlenmeyer flask and saturate with H_2S (E). Note the general appearance of the precipitate. Shake and filter, and try the solubility of the precipitate in cold dilute HNO_3 (?). Reserve the precipitate for the next test.

3. *Reaction of Sulfides with Nitric Acid.*—Boil the HNO_3-Ag_2S mixture from the preceding experiment (E). Why is the sulfur residue not yellow?

Note.—The separation of impure sulfur when many substances, particularly ores, are treated with HNO_3 is strongly indicative of the presence of sulfides.

4. *The Lead Acetate Test for Hydrogen Sulfide.*—Moisten a piece of filter paper with a drop or two of $Pb(C_2H_3O_2)_2$ solution, and allow H_2S to come in contact with it (?, E).

5. *Test for Insoluble Sulfides.*—Place a little powdered iron pyrites, FeS_2, in a beaker, cover with water, and add dilute HCl. Cover the beaker with a piece of filter paper moistened with a drop or two of $Pb(C_2H_3O_2)_2$ solution and a watch glass and warm (?). Now add a little zinc dust (?, E).

Note.—This effect is explained as due to the "nascent" hydrogen, formed by the action of the Zn and HCl, reducing the FeS_2 to FeS and H_2S. See **(18,** 4) for comment on the theory of nascent action.

GROUP II

This group contains the anions whose Ag^+ salts are only slightly soluble in cold water, but are readily soluble in dilute HNO_3; and whose Ba^{++} salts are soluble in water: NO_2^-, $C_2H_3O_2^-$, and OH^- (or O^{--}).

On account of the appreciable solubility of $AgNO_2$ and $AgC_2H_3O_2$ in water, they might also be considered members of Group IV, and in actual analysis it is good practice to test for them along with the members of that group.

PRELIMINARY EXPERIMENTS

(87) Nitrite, NO_2^-. 1. *Reaction with Acids.*—To a little solid potassium nitrite, KNO_2 (sodium nitrite, $NaNO_2$, may be used),

in a test tube, add dilute H_2SO_4. The primary action forms HNO_2 (E), which is unstable and decomposes into water and oxides of nitrogen (E).

2. *Reaction with Ferrous Sulfate.*—Dilute 1 cc. of KNO_2 solution and add $FeSO_4$ solution (?). The brown color is due to an unstable compound of the approximate composition, $FeSO_4.NO$. Assuming free H_2SO_4 to be present, complete and balance the following equations:

$$KNO_2 + H_2SO_4 \rightarrow HNO_2, \text{ etc.}$$
$$HNO_2 + FeSO_4 + H_2SO_4 \rightarrow NO + Fe_2(SO_4)_3, \text{ etc.}$$
$$NO + FeSO_4 \rightarrow$$

(88) **Acetate, $C_2H_3O_2^-$.** 1. *Reaction with Concentrated Sulfuric Acid.*—Place a little solid sodium acetate, $NaC_2H_3O_2$, in a test tube, moisten with a drop of water, and add concentrated H_2SO_4 (E). Note the vinegar-like odor.

2. *The Ethyl Acetate Test.*—To a little $NaC_2H_3O_2$ solution in a test tube add about 5 cc. of alcohol-H_2SO_4 mixture, and warm. The more or less pleasant odor is that of ethyl acetate, $C_2H_5.C_2H_3O_2$, which is formed thus: $C_2H_5OH + HC_2H_3O_2 \rightarrow C_2H_5.C_2H_3O_2 + H_2O$. Suggest one function of the concentrated H_2SO_4 in this reaction (?).

(89) **Hydroxide, OH^-.** 1. *Heat of Neutralization.*—Place a little dilute NaOH solution in a test tube, and, holding the tube in the palm of the hand, add a dilute acid—*e.g.*, dilute H_2SO_4 (?). Explain the effervescence when concentrated acids are added to bases, as HCl to solid CaO (?).

2. *Tests for Hydroxide.*—There are many delicate tests for the presence of OH^- in a solution, as the turning of red litmus blue, or colorless phenolphthalein red, etc. These tests are not distinctive, however, in that the hydroxyl group may have come from the water (*hydrolysis*), and not from the solid substance. Unfortunately, there is no direct test for hydroxides (and oxides) in the solid state.

GROUP III

This group contains the anions whose Ag^+ and Ba^{++} salts are insoluble in water, but soluble in dilute HNO_3: CO_3^{--},

$C_2O_4^{--}$, $C_4H_4O_6^{--}$, SO_3^{--}, $S_2O_3^{--}$, AsO_3^{---}, AsO_4^{---}, PO_4^{---}, BO_3^{---}, CrO_4^{--}.

On account of the importance of the colors of the Ag^+ salts in indicating what anions may be present, particular attention should be given to the color of the precipitate obtained with $AgNO_3$ solution.

There are a number of interferences in this group which the student should keep in mind: Carbonates must be removed before testing for oxalates; arsenates must be removed before testing for phosphates; thiosulfates interfere with the test for sulfite; and sulfites and thiosulfates sometimes interfere with the test for carbonates.

PRELIMINARY EXPERIMENTS

(90) Carbonate, CO_3^{--}. 1. *Reaction with Acids.*—Place a little solid sodium carbonate, Na_2CO_3, in a beaker and add dilute H_2SO_4 (?, E). Repeat, using powdered dolomite, $CaCO_3$.-$MgCO_3$, instead of Na_2CO_3. Compare the vigor of the reactions (?).

2. *The Lime Water Test.*—Dip a piece of glass tubing in some calcium hydroxide solution, $Ca(OH)_2$, in a test tube, and hold it in the gases evolved in the above experiments. What is the white film that forms on the drop (E)? In which case is this test apt to be uncertain?

Place a little powdered dolomite in a test tube fitted with a thistle tube and a delivery tube (see Fig. 9). Introduce water until the end of the thistle tube is covered, and then add dilute H_2SO_4.

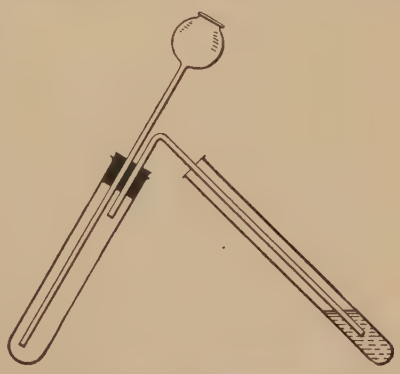

FIG. 9.—Test tube generator for liberation of CO_2.

Heat the generator tube over a low flame until the solution boils, bubbling the gas evolved through a little $Ca(OH)_2$ solution in a second test tube. The steam sweeps over the CO_2 and makes the test more sensitive.

What is the result if CO_2 *in excess* is passed into $Ca(OH)_2$ (E)?

3. *Color of Silver Carbonate.*—To a little dilute $AgNO_3$ solution add Na_2CO_3 solution (E). Note the color of the precipitate (?).

(91) Oxalate, $C_2O_4^{--}$. 1. *Reactions with Sulfuric Acid.* Place a little solid sodium oxalate, $Na_2C_2O_4$, in a test tube, add dilute H_2SO_4 and warm (?).

Note.—This reaction gives a means of separating oxalates from carbonates, as the latter are completely decomposed upon heating with dilute acids.

Place a little solid $Na_2C_2O_4$ in a test tube, add concentrated H_2SO_4, and warm until a vigorous effervescence begins (E). Set fire to the gas at the mouth of the tube, and note the color of the flame (?).

2. *Oxidation of Oxalic Acid by Manganese Dioxide.*—Place a little pure manganese dioxide, MnO_2, in the test tube generator outfit used in (**90**, 2), and add a little ammonium oxalate solution, $(NH_4)_2C_2O_4$, and enough water to cover the end of the thistle tube. Acidify with dilute H_2SO_4 (E) and heat as in (**90**), passing the gas evolved into $Ca(OH)_2$ solution (?).

3. *Color of Silver Oxalate.*—Add a few drops of $(NH_4)_2C_2O_4$ solution to some $AgNO_3$ solution (E). Note the color of the precipitate.

***(92) Tartrate, $C_4H_4O_6^{--}$.** 1. *Carbonization.*—Heat a little solid tartaric acid, $H_2C_4H_4O_6$, in a hard glass test tube (?). Note the odor (?).

2. *Color of Silver Tartrate.*—Add a few drops of $AgNO_3$ solution to some Rochelle salts solution, $KNaC_4H_4O_6$ (E). Note the color of the precipitate (?).

3. *Solubility of Calcium Tartrate.*—To some $KNaC_4H_4O_6$ solution add $CaCl_2$ solution (E). Filter, place the precipitate in a test tube, and NaOH solution, and shake well (?). Dilute with an equal volume of water, filter, and boil the filtrate (?).

4. *The Silver Mirror.*—Clean a test tube by boiling in it, first a little NaOH solution, and then some concentrated HNO_3. Wash well with water, and introduce a few cubic centimeters of $AgNO_3$ solution. Dilute some NH_4OH with several volumes of water, and add this, drop by drop, to the $AgNO_3$ solution until a turbid precipitate of Ag_2O just forms. Add a little NaOH solution and then some $KNaC_4H_4O_6$ solution, and place the tube in a beaker of boiling water for several minutes (?).

Note.—The Rochelle salt solution reduces Ag^+ to Ag. No equation is to be written.

(93) Sulfite, SO_3^{--}. 1. *Reaction with Acids.*—Dissolve a little sodium sulfite, Na_2SO_3, in water, and add dilute HCl (E). Cautiously try the odor of the mixture (?). Save the solution for the next test.

2. *Reducing Action of Sulfurous Acid on Potassium Permanganate Solution.*—Dilute 1 drop of $KMnO_4$ solution to about 5 cc., and add the solution of H_2SO_3 from the above test (?). To the clear solution add dilute HNO_3 and $Ba(NO_3)_2$ solution (the reagent for the SO_4^{--} ion) (?). Write the equation for the reaction between $KMnO_4$ and H_2SO_3 solutions (E).

3. *Color of Silver Sulfite.*—Dissolve a pinch of Na_2SO_3 in water, and divide the solution into two parts. Save one portion for the next test. To the other portion add a drop or two of $AgNO_3$ solution (E). Note the color of the precipitate (?).

4. *Oxidation of Dry Sodium Sulfite.*—Test the remaining portion of the Na_2SO_3 solution for SO_4^{--} with a few drops of $Ba(NO_3)_2$ solution. A white precipitate, insoluble in HNO_3, indicates SO_4^{--}. The presence of sulfate seems to be due to atmospheric oxidation.

(94) Thiosulfate, $S_2O_3^{--}$. 1. *Reaction with Acids.*—Acidify a little sodium thiosulfate solution, $Na_2S_2O_3$, with dilute HCl. Note precipitate and odor, and write the equation (E).

2. *Color of Silver Thiosulfate.*—To a little $AgNO_3$ solution add a single drop of $Na_2S_2O_3$ and shake promptly (E). What is the color of the precipitate just after its formation?

Note.—Silver thiosulfate undergoes hydrolysis, particularly upon heating, according to the equation: $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$.

(95) Arsenite, AsO_3^{---}, and Arsenate, AsO_4^{---}. 1. *Color of Silver Arsenite and Silver Arsenate.*—To small amounts (in separate test tubes) of solutions of sodium arsenite, Na_3AsO_3, and of potassium arsenate, K_3AsO_4, add $AgNO_3$ solution. Write equations (E's), labeling the precipitates with names and colors.

2. *Reaction of Arsenates with Ammonium Molybdate.*—To a little K_3AsO_4 solution add 5 cc. of *clear* $(NH_4)_2MoO_4$ solution (in HNO_3)—the test reagent for PO_4^{---}—and warm (?).

3. *Separation of Arsenates and Phosphates.*—Recall the precipitation of arsenic sulfides by H_2S in the presence of HCl and NH_4I. (See (**24**, 2), page 19.)

(**96**) **Phosphate, PO_4^{---}.** 1. *Color of Silver Phosphate.*—To some dilute $AgNO_3$ solution add a drop or two of sodium phosphate solution, Na_2HPO_4 (E). Note the color of the precipitate (?).

2. *Reaction with Ammonium Molybdate.*—Dilute 1 cc. of Na_2HPO_4 solution with 3 or 4 volumes of water, and add 5 cc. of $(NH_4)_2MoO_4$ solution (in HNO_3) and warm (E). The precipitate has the approximate formula, $(NH_4)_3PO_4.12MoO_3$.

Repeat the test, adding 2 or 3 cc. of dilute HCl before introducing the $(NH_4)_2MoO_4$ reagent (?). Is the test for phosphates sensitive in the presence of chlorides?

(**97**) **Borate, BO_3^{---}.** 1. *Color of Silver Borate.*—To a solution of borax, $Na_2B_4O_7$, add a few drops of $AgNO_3$ solution. The formula of the precipitate is written $AgBO_2$. Write equation (E), and label the precipitate with its color (?).

2. *The Turmeric Reaction.*—Moisten a piece of turmeric paper (storeroom) with some $Na_2B_4O_7$ solution which has been acidified with HCl, and dry it on a watch glass over a beaker of boiling water (?). Touch the paper with a drop of diluted NaOH solution on a stirring rod (?).

3. *The Flame Test.*—Put a little powdered borax in a porcelain dish and add 5 cc. of alcohol-concentrated H_2SO_4 mixture. Warm and set fire to the vapors (?). The color is due to the presence of ethyl borate, $(C_2H_5)_3BO_3$. Write equations for the preparation of ethyl borate in steps as follows: (1) action between $Na_2B_4O_7$ and H_2SO_4 (assuming the presence of a little water); (2) action between C_2H_5OH and one of the products.

(**98**) **Chromate, CrO_4^{--}, and Dichromate, $Cr_2O_7^{--}$.** 1. *Color of Silver Chromate.*—To a little $AgNO_3$ solution add a drop or two of potassium chromate solution, K_2CrO_4 (E). Note the color of the precipitate (?).

2. *Reduction by Hydrogen Sulfide.*—Recall the action of H_2S on a solution of $K_2Cr_2O_7$ acidified with HCl. (See (**43**, 4), page 38.)

3. *Equilibrium between Chromate and Dichromate.*—What happens when K_2CrO_4 solution is acidified, *e.g.*, with H_2SO_4 (?, E)?

When $K_2Cr_2O_7$ solution is made alkaline with KOH solution (?, E)? Why is HCl not used in converting a chromate into a dichromate (?, E).

Note.—The equilibrium between chromate and dichromate might be expressed by an ionic equation, thus: $2CrO_4^{--} + 2H^+ \rightleftarrows Cr_2O_7^{--} + H_2O$. From this it follows that chromates can exist only in neutral or alkaline solution, and dichromates only in acid solutions.

4. *The Hydrogen Peroxide Test.*—Recall the action of hydrogen peroxide, H_2O_2, with acidified solutions of chromates (or dichromates) in the presence of ether. (See (**43,** 3), page 38.)

GROUP IV

This group contains those anions whose Ag^+ and Ba^{++} salts are soluble in water: NO_3^-, ClO_3^-, MnO_4^-. On account of the very appreciable solubility of silver nitrite and silver acetate in water, NO_2^- and $C_2H_3O_2^-$ may, in practice, be considered as belonging to this group.

Since $AgNO_3$ and $Ba(NO_3)_2$ solutions give no information about the presence or absence of this group, it is necessary, in a complete analysis, to make separate tests for each member in every unknown.

PRELIMINARY EXPERIMENTS

(**99**) **Nitrate, NO_3^-.** 1. *Reaction with Concentrated Sulfuric Acid.*—Place a little solid sodium nitrate, $NaNO_3$, in a test tube, moisten with a drop of water, and add concentrated H_2SO_4 (E). Are brown fumes[1] evolved? Compare the amount with that given off with nitrite, (**87,** 1), page 79.

Note.—Nitric acid in concentrated form is somewhat unstable, decomposing to a small extent in the cold, according to the equation: $4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2$.

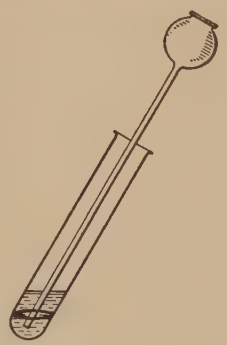

FIG. 10.—The "brown ring" test.

2. *Reaction with Ferrous Sulfate.*—Dilute 2 or 3 drops of $NaNO_3$ solution to 3 cc., add an equal volume of saturated $FeSO_4$ solution, and acidify with dilute H_2SO_4 (?). Compare nitrite, (**87,** 2) page 80. By means of a thistle tube introduce con-

[1] Best seen by looking down through the tube.

centrated H_2SO_4 below the mixture, tilting the tube considerably (see Fig. 10) so that the acid will not carry down bubbles of air and stir the mixture. The brown ring formed at the junction of the two layers contains $FeSO_4.NO$. Complete and balance the following equations for the consecutive reactions involved in the test:

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3, \text{ etc.}$$
$$FeSO_4 + H_2SO_4 + HNO_3 \rightarrow Fe_2(SO_4)_3 + NO, \text{ etc.}$$
$$FeSO_4 + NO \rightarrow$$

*(**100**) **Chlorate, ClO_3^-.** 1. *Reaction with Concentrated Sulfuric Acid.*—Place a minute amount of solid potassium chlorate, $KClO_3$, in a test tube, and add concentrated H_2SO_4 (?). (Be careful not to hold the face over the tube.) Write the equation for the primary action producing chloric acid, $HClO_3$ (E).

Note.—$HClO_3$ is exceedingly unstable and decomposes (sometimes with violence) as follows: $3HClO_3 \rightarrow HClO_4 + 2ClO_2 + H_2O$. The yellow-green gas, chlorine dioxide, ClO_2, is soluble in concentrated H_2SO_4, giving a yellow solution.

(**101**) **Permanganate, MnO_4^-.** 1. *Reduction of Permanganic Acid by Hydrogen Sulfide.*—Recall the action of H_2S on an acidified solution of $KMnO_4$. (See (**27**, note 2), page 25.)

GROUP V

This group contains the anions whose Ag^+ salts are soluble in water, and whose Ba^{++} salts are insoluble in water: SO_4^{--}, F^-. $BaSO_4$ is insoluble in HCl and in HNO_3, while BaF_2 is moderately soluble in these acids.

PRELIMINARY EXPERIMENTS

(**102**) **Sulfate, SO_4^{--}.** 1. *Formation of Barium Sulfate.*—Dilute a few drops of potassium sulfate solution, K_2SO_4, and add $Ba(NO_3)_2$ solution (E). Try the solubility of the precipitate in HCl or in HNO_3 (?).

Note.—$BaCl_2$ solution is frequently used as a reagent for SO_4^{--}, but $Ba(NO_3)_2$ seems preferable for the following reason: With Ag^+, Hg_2^{++}, and Pb^{++}, $BaCl_2$ precipitates insoluble chlorides which might be mistaken for $BaSO_4$. $Ba(NO_3)_2$, on the other hand, may be used in all cases, since all nitrates are soluble.

2. *Precipitation of Barium Nitrate by Nitrates.*—Place a few cubic centimeters of the reagent $Ba(NO_3)_2$ solution in a test tube and add a little concentrated HNO_3. What is the precipitate? Explain its formation (?). Try to dissolve it by adding water and warming (?).

Note.—This is another phase of the "common ion effect." The equilibria in a saturated solution of $Ba(NO_3)_2$ containing some of the solid salt may be represented: $Ba(NO_3)_2$ (solid) $\rightleftarrows$ $Ba(NO_3)_2$ (dissolved) $\rightleftarrows$ $Ba^{++} + 2NO_3^-$. When any solution containing a still higher concentration of NO_3^- (as concentrated HNO_3) is added, the equilibria are shifted to the left, with the formation of more precipitate. This is what happens in the above experiment, in which the $Ba(NO_3)_2$ is practically a saturated solution.

It will be seen that the "common ion effect" in this case operates to diminish the solubility of $Ba(NO_3)_2$. The phenomenon is quite general, and advantage is taken of this effect to make precipitations more complete by adding an excess of the precipitating agent. For example, excess of HCl is used in precipitating Cation Group I to diminish the solubility of $PbCl_2$, excess of $HClO_4$ is used in the precipitation of K^+ to reduce the solubility of $KClO_4$, etc.

* **(103) Fluoride, F^-.** 1. *Precipitation of Calcium Fluoride.*—To a little sodium fluoride solution, NaF, add $CaCl_2$ solution (E). Try the solubility of the precipitate in HCl or HNO_3 (?).

2. *Reaction with Sulfuric Acid and Silica.*—Place a little powdered calcium fluoride, CaF_2, in a dry test tube, moisten with a drop of water, and add concentrated H_2SO_4. Write the equation for the reaction between the fluoride and the acid, and a second equation for the reaction of one of the products with the SiO_2 of the glass. Warm gently and hold just above the surface of the mixture a piece of glass tubing carrying a drop of water (?). The precipitate which forms in the drop is silicic acid, which may here be written $Si(OH)_4$. Carefully clean and dry the test tube, and examine it to see whether it has been etched.

Note.—The H_2F_2, formed in the primary reaction reacts with the silica, SiO_2, of the glass of the test tube, giving the gaseous silicon tetrafluoride, SiF_4. This is hydrolyzed on coming in contact with the drop of water, as follows: $3SiF_4 + 4H_2O \rightarrow 2H_2SiF_6 + Si(OH)_4$.

GROUP VI

This group contains the anions of non-volatile acids which form soluble salts with the alkali cations only. These anions

are not amenable to classification by their behavior with $AgNO_3$ and $Ba(NO_3)_2$, not only because of the small number of soluble salts formed, but because they form upon acidification unstable acids producing insoluble residues.

The only member of this group occurring in the commoner materials is silicate, usually written SiO_3^{--}. Silicon dioxide, SiO_2, is the anhydride of a number of more or less hypothetical silicic acids, which are known only by their salts. As just stated, the alkali silicates, Na_2SiO_3 and K_2SiO_3, are the only soluble silicates. The others are practically insoluble in all acids except hydrofluoric, H_2F_2.

PRELIMINARY EXPERIMENTS

***(104) Silicate, SiO_3^{--}.** 1. *Precipitation of Silicic Acid.*—Place a little sodium silicate solution, Na_2SiO_3 (also called "water glass"), in a beaker, and slowly acidify with dilute HCl, stirring during the addition of the acid (E). Is the precipitate crystalline or colloidal? Evaporate some of the mixture containing the precipitate to dryness in a Pyrex beaker. Add water. Will the precipitate pass again into the colloidal state?

2. *Reaction with the Sodium Carbonate Bead.*—(Instructions.) Make a small loop in a clean platinum wire, heat and bring the hot wire in contact with some anhydrous Na_2CO_3 on a watch glass. Some of the powder will adhere to the wire. Heat again and continue adding carbonate until a perfectly clear bead 2 or 3 mm. in diameter is obtained. Touch the hot bead to a *minute* amount of pure silica, SiO_2, on a watch glass, and heat again (?, E). Explain the transparency of the bead and the effervescence (?).

Note.—The platinum wire may be easily cleaned by heating the bead to redness and dipping the bead into cold water. The bead is shattered, and the fragments may be easily separated from the wire without injuring it.

3. *Reaction with the Metaphosphate Bead.*—Prepare a bead as in the preceding experiment, only using microcosmic salt, $NaNH_4HPO_4$, instead of Na_2CO_3. Upon heating, this material loses NH_3 and H_2O, leaving a glassy mass of sodium metaphosphate, $NaPO_3$. Touch the hot bead to a minute amount of SiO_2 on a watch glass and heat again. Does the SiO_2 dissolve? The opaque mass is known as a "silica skeleton."

Exercises

1. How do non-metals usually occur in analytical materials?
2. What two solutions are used as reagents in classifying anions into groups?
3. List the anions which give yellow-to-brown fumes with hot concentrated H_2SO_4.
4. List the Ag^+ salts under their color: white, yellow, red, brown, black.
5. List the unstable acids; that is, the acids which decompose spontaneously in the pure state.
6. List the volatile acids; that is, the acids which may be expelled from their salts by heating with concentrated H_2SO_4.
7. Give the colors conferred on CS_2 by the free halogens.
8. Could an acid solution containing I^- also contain NO_2^-? Why?
9. What ions could be present in a neutral solution containing Ag^+ and Ba^{++}?
10. List the acids which reduce concentrated H_2SO_4.
11. How would a bromide (*e.g.*, KBr) react if the chromyl chloride test were made on it?
12. What substances besides Fe^{+++} give a red color with SCN^-? What substances besides SCN^- give a red color with Fe^{+++}?
13. An unknown substance reacts with HNO_3, leaving a yellow, gummy residue which tends to float in the acid solution. Interpret.
14. What is the effect of Na_2CO_3 solution on litmus and phenolphthalein? Explain.
15. How could you distinguish between dry CaO and dry $Ca(OH)_2$?
16. In the test for CO_3^{--} in an unknown, a white precipitate formed in the lime water, but later redissolved. Was a carbonate present?
17. How could KNO_2 and KNO_3 be distinguished by means of the $FeSO_4$ test?
18. What anion other than CO_3^{--} sometimes gives, upon acidification with dilute H_2SO_4, a positive lime water test?
19. Give an easy way for removing $CaCO_3$ from a mixture of CaC_2O_4 and $CaCO_3$.
20. How could SO_2 be removed from a mixture of SO_2 and CO_2?
21. How could an arsenate be distinguished from a phosphate?
22. Give quick methods for distinguishing between (*a*) Na_2CO_3 and Na_2SO_3, (*b*) Na_2SO_3 and $Na_2S_2O_3$, (*c*) K_3AsO_3 and K_3AsO_4.
23. Suggest how the presence of SO_4^{--} would vitiate the turmeric test for BO_3^{---}.
24. Explain how water solutions of chromates can be distinguished from dichromates by means of litmus paper.
25. List the anions that could be present in an acidified solution containing MnO_4^-.
26. Is a precipitate with $BaCl_2$ solution, insoluble in water and HNO_3, a test for SO_4^{--}? Recall the reaction between $BaCl_2$ and $AgNO_3$ solutions. Cite two other similar cases.

27. List the anions whose acids are (*a*) strong oxidizing agents, (*b*) strong reducing agents. Would it be expected (with certain limitations) that acid solutions would contain representatives of both lists?

28. A neutral solution gives no precipitate with $AgNO_3$ solution, but a white precipitate with $Ba(NO_3)_2$ solution, soluble in excess of strong HNO_3. What anion would be suspected?

29. An alkaline solution gives, upon acidification with HCl, a white gelatinous precipitate, insoluble in NaOH solution after evaporation. Identify the anion.

30. What difference in property of the acid anhydrides accounts for the fact that SiO_2 will dissolve in the Na_2CO_3 bead, but not in the $NaPO_3$ bead?

31. What is impossible in each of the following reports on the analyses of unknown solutions? (*a*) KI, KNO_2, $H_2C_2O_4$; (*b*) $FeSO_4$, $NaNO_2$, $HC_2H_3O_2$; (*c*) $K_2Cr_2O_7$, Na_2S, H_2SO_4; (*d*) Na_2SO_3, $KMnO_4$, H_2SO_4; (*e*) $KClO_3$, KI, HCl.

ANALYSIS[1]

The analytical procedure for anions, particularly in simple substances where only one or two anions are present, may be shortened considerably by taking advantage of the information furnished by such considerations as (1) reaction of the dry substance with concentrated sulfuric acid, (2) presence of free acid, and (3) solubility of the substance and the nature of the cations present.

Concentrated sulfuric acid reacts with solids (or, better, solids moistened with a drop of water), liberating volatile acids (*e.g.*, hydrochloric, acetic, etc.) and decomposing unstable acids (hydriodic, nitrous, thiosulfuric, etc.), with the formation of products more or less easily recognized.

Strongly acid solutions, as a general rule, will not contain the anions of the unstable or very volatile acids, *viz.*: S^{--}, NO_2^-, SO_3^{--}, CO_3^{--}, $S_2O_3^{--}$, and ClO_3^-. This is particularly true of solutions which have stood in contact with the air for some time, as is the case with the unknown solutions issued in courses in Qualitative Analysis. On the other hand, the analysis of industrial products affords frequent exceptions to this rule, particularly in the cases of SO_3^{--} and CO_3^{--}; for example, "bisulfite liquor" used in preparing wood pulp for paper making contains SO_3^{--}

[1]This procedure for the detection of anions is an enlargement of the one devised by the author and published in his revision of W. A. Noyes' "Qualitative Analysis," 7th edition (Henry Holt & Co.).

in acid solution. A fairly safe rule is that anions of unstable[1] or volatile[2] acids will probably be absent in solutions acid enough to give a yellow color with methyl violet pencil marks.

Solubility considerations are very valuable in indicating the presence or absence of various anions. When a neutral solution is found to contain a certain cation, the anions which form insoluble salts with that ion may be generally assumed to be absent. For example, if a neutral solution is found to contain Ba^{++}, it could not contain AsO_3^{---}, AsO_4^{---}, PO_4^{---}, BO_3^{---}, $C_2O_4^{--}$, F^-, CO_3^{--}, SiO_2^{--}, or $C_4H_4O_6^{--}$, since all of these form Ba^{++} salts insoluble in water.

Note.—The student is warned not to accept this statement as infallible. There are a number of cases where salts insoluble in water dissolve readily in solutions of certain salts; *e.g.*, $MgCO_3$ in NH_4Cl, $PbSO_4$ in $NH_4C_2H_3O_2$, $AgBr$ in $Na_2S_2O_3$, CuC_2O_4 in $Na_2C_2O_4$, etc. This phenomenon is due to the formation of complex ions or molecules of low ionization. The following of the commoner ions may be noted as given to forming such complexes: NH_4^+, CN^-, $C_2H_3O_2^-$, $C_2O_4^{--}$, $C_4H_4O_6^{--}$, $S_2O_3^{--}$.

(105) General Procedure.—1. Carry out the regular analysis for cations, (**14**) to (**78**).

Note.—This step is necessary, not only for the detection of arsenite, arsenate, permanganate, chromate, and dichromate, but it places the analyst in a position to interpret certain solubility relations. (See 4, below.)

2. Place a little of the solid substance in a test tube, moisten with a drop of water, and add concentrated H_2SO_4. In case of a solution, evaporate a portion of it nearly to dryness in a casserole and then add concentrated H_2SO_4. If effervescence occurs, the anions of one or more of the volatile or unstable acids are present (see Preliminary Experiments (**79**) to (**104**)); if there is no effervescence, even on heating, the following anions only can be

[1] Unstable acids, strictly speaking, decompose whenever the attempt is made to prepare them, either in solution or in the anhydrous state. They are HNO_2, H_2SO_3, H_2CO_3, $H_2S_2O_3$ and $HClO_3$. The term is here extended to include also those acids which are decomposed by the oxidizing or dehydrating action of concentrated H_2SO_4; *e.g.*, HBr, HI, H_2S, $H_2C_2O_4$ and $HMnO_4$.

[2] Acids having a lower boiling point than H_2SO_4 are classed as volatile. They are HCl, HBr, HI, HCN, H_2S, HNO_3 and H_2F_2. H_3BO_3 is volatile in steam.

present: PO_4^{---}, AsO_3^{---}, AsO_4^{---}, CrO_4^{--}, BO_3^{---}, SO_4^{--}, and SiO_3^{--}. (See Table XV.)

TABLE XV.—REACTIONS OF ANIONS WITH CONCENTRATED SULFURIC ACID

No effect	Gas liberated		
	Color	Reactions of gas	Anions indicated
Anions that may be present:	Colorless	White precipitate with $AgNO_3$.	Cl^-
	Colorless	Brown stain on $Pb(C_2H_3O_2)_2$ paper.	S^{--}
PO_4^{---},	Colorless	Characteristic odor with alcohol.	$C_2H_3O_2^-$
AsO_3^{---},	Colorless	Odor of SO_2 { No S is liberated.	SO_3^{--}
AsO_4^{---},		{ S is liberated.	$S_2O_3^{--}$, S^{--}
CrO_4^{--},	Colorless	White precipitate with $Ca(OH)_2$.	CO_3^{--}, $C_2O_4^{--}$
BO_3^{---},	Colorless	Tube is etched; turbidity in drop of water.	F^-
MnO_4^-,			
SO_4^{--},	Colorless	Gas burns with a blue flame.	$C_2O_4^{--}$,
SiO_3^{--}.			$Fe(CN)_6^{---}$,
			$Fe(CN)_6^{----}$
	Colorless	Disagreeable odor and separation of S.	SCN^-
	Greenish-yellow	Yellow color in H_2SO_4; explosion upon warming.	ClO_3^-
	Brown	Creamy precipitate with $AgNO_3$; red litmus paper is bleached.	Br^-
	Brown	Brown color in drop of $FeSO_4$.	NO_2^-, NO_3^-
	Purple	Blue color with starch paper.	I^-

3. If the substance is a solid, use a small portion to find out whether it is soluble in water[1] or in acids; if it is a solution, test for the presence of free acids[2] by placing a drop on a scratch mark made by a "copying" (*i.e.*, methyl violet) pencil on a piece

[1] Determined by placing a small amount of the substance in a test tube, adding water, and warming. In case of doubt as to the result, filter and evaporate some of the filtrate to dryness in a small beaker. A residue indicates solubility. If partial solution has been effected, add more water and heat again. If the residue appears insoluble in water, the substance is probably a mixture. In that case consider it an "acid-soluble" unknown.

[2] If the solution is strongly acid, the following anions cannot be present, since the corresponding free acids are either volatile or else unstable: S^{--}, NO_2^-, CO_3^{--}, $S_2O_3^{--}$, CN^-, and ClO_3^-.

of glazed paper. If a green-to-yellow color is produced, the presence of free acids is indicated. If the substance can be neutralized by dilute NaOH or NH_4OH (by slowly adding the base until the solution gives a violet color with the pencil marks) without forming a precipitate, the original solid is soluble in water.

4. From the solubility Table, page 122, infer what anions might be present with the cations already found so as to fulfil the solubility conditions found in the preceding paragraph.

Note.—A number of salts usually thought of as soluble are not strictly so, since they undergo hydrolysis to a greater or less extent, giving insoluble products. For example, $SbCl_3$ gives insoluble SbOCl; $SnCl_4$ gives insoluble $Sn(OH)_4$; $FeCl_3$ gives insoluble $Fe(OH)Cl_2$ upon boiling; $Pb(C_2H_3O_2)_2$ gives insoluble $Pb(OH)_2.2PbCO_3$ (due to CO_2 in the water), etc.

5. Classify the substance under one of the following cases, and follow the procedure indicated.

Case I.—The substance is a solid soluble in water, or a neutral solution, and contains no cations other than Na^+, K^+, and NH_4^+.

Test separate portions of the substance for Group I by (**106**), Group V by (**130**), and Group III by (**118**). If any one of these groups is indicated, test separate portions of the substance for the ions of that group.

Test for the ions of Group II by (**114**) and (**115**), of Group IV by (**127**) to (**129**), and of Group VI by (**133**).

Case II.—The substance is a solid soluble in water, or a solution neutral to methyl violet, and contains cations other than Na^+, K^+, and NH_4^+. Use Method *A* or Method *B*.

Method *A*.—Infer from the Solubility Table, page 122, what anions could be present in a water solution containing the ions found in the cation analysis. Test separate portions of the substance for these possible ions without attempting to ascertain the anion groups present.

Note.—Bear in mind the solvent action of certain salt solutions on certain substances insoluble in water. (See page 91.)

Method *B*.—Test portions of the unknown substance for Group I by (**106**) and for Group V by (**130**). From another portion remove the ions of the Cation Groups I, II, III, and IV by (**117**) and test the solution obtained for the presence of Anion Group

III by (**118**). Test separate portions of the original substance for the anions of the groups indicated. Also make tests for the anions of Groups II and IV, and (if an acid was used to bring the substance into solution) the anions which form unstable acids, *viz.:* CO_3^{--}, SO_3^{--}, $S_2O_3^{--}$, S^{--}, etc.

Case III.—The substance is a solid insoluble in water, but soluble in strong acids; or it is a strongly acid solution.[1]

Test a portion for Anion Group I by (**106**) and another portion for Group V by (**130**). Test for the individual members of the groups indicated.

TABLE XVI.—PROCEDURES IN ANION ANALYSIS

Cations found in metallic ion analysis	Nature of the unknown substance			
	Solid, soluble in water, or in neutral solution	Acid solution	Solid, soluble in acids	Solid, insoluble in acids
Na^+, K^+, NH_4^+.	All the anions may be present. *Follow Case I*	Anions which may be present: Group I (except CN^-, S^{--}) Group II (except NO_2^-) Group III (except CO_3^{--}, SO_3^{--}, $S_2O_3^{--}$) Group IV (except ClO_3^-) Group V (SO_4^{--} only, if in glass vessel) *Follow Case III*		
Cations of Groups I, II, III, IV, V.	Only those anions may be present which form soluble salts with the cations present. For exceptions see page 91. *Follow Case II*		All anions may be present except those which form with cations present salts insoluble in acids. *Follow Case III*	Only those anions may be present which form with cations present salts insoluble in acids. *See "Systematic Analysis"*

[1] The student should bear in mind that certain anions are not to be expected in strongly acid solutions. (See page 90.)

Remove Cation Groups I, II, III, and IV by (**117**), and test for the presence of Anion Group III by (**118**). If the group is indicated, test only for the anions of the stable acids; *i.e.*, for $C_2O_4^{--}$, $C_4H_4O_6^{--}$, BO_3^{---}, AsO_3^{---}, AsO_4^{---}, PO_4^{---}, and CrO_4^{--}. If the substance was an acid-soluble solid, be sure to make tests for the other members of Group III on portions of the original substance.

Test[1] separate portions of the original substance for the members of Anion Groups II and IV.

Case IV.—The substance is insoluble in acids. See "Systematic Analysis," page 109.

Group I

(**106**) **Test for Group I; Chloride.**—To a solution of the unknown substance add dilute HNO_3 (if not already present) and $AgNO_3$ solution. Shake well, filter, and reserve the filtrate for (**118**). A precipitate indicates the presence of the anions of Group I. Note the color and the general appearance of the precipitate, and infer what anions are indicated.

A white precipitate (in the absence of CN^-, SCN^-, and $Fe(CN)_6^{----}$)[2] indicates Cl^-. If the precipitate is not white, see (**107**) and (**113**).

(**107**) **Iodide.**—Acidify a portion of the solution of the unknown substance with an excess of dilute H_2SO_4 and add 1 cc. of CS_2 and a little KNO_2 solution and shake. A purple color in the CS_2 layer indicates the presence of I^- in the original solution.

If bromides may also be present, filter through a wet filter paper, in order to remove the CS_2. Heat the filtrate and test for the completeness of the action by adding more KNO_2 solution. When the action is complete, boil until starch paper[3] held in the steam no longer turns blue. When the iodine is completely expelled, divide the solution into two parts, reserving one portion for (**108**) and the other for (**109**).

[1] Only when the substance is partially soluble in water is this step necessary. If the substance is wholly insoluble in water, none of the anions of these groups could be present.

[2] For the removal of these interfering ions, consult an advanced manual on Qualitative Analysis.

[3] Strips of filter paper that have been dipped in starch solution. If dried, this paper will keep indefinitely.

(108) **Bromide.**—To one-half of the filtrate from (107) add 1 cc. of CS_2, and then chlorine solution, Cl_2, and shake well. A brown color in the CS_2 layer indicates Br^-.

A purple color in the CS_2 indicates the incomplete removal of the iodide. In this case continue the addition of Cl_2, with vigorous and persistent shaking, until the purple color is bleached out. A final brown color indicates Br^-.

Note.—Excess of Cl_2 oxidizes I_2 to HIO_3, which gives no color to CS_2. The equation for this oxidation is: $I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$.

*(109) **Chloride in the Presence of Bromide and Iodide.**—Neutralize the second portion of the solution from (107) by NaOH solution (litmus test) and evaporate to dryness. By means of a spatula transfer the residue to a mortar, add about twice its amount of solid $K_2Cr_2O_7$, and grind together. Place the mixture, along with a piece of porous tile (to prevent bumping), in a 50-cc. distilling flask (storeroom), and cover with concentrated H_2SO_4. Cork the flask, place a test tube containing 2 or 3 cc. of water over the side neck (see Fig. 7), and distil as long as brown fumes come over. (*The delivery tube should not dip under the water. Such an arrangement would be dangerous.*) Add to the distillate an equal volume of $NaC_2H_3O_2$ solution, and a few drops of $Ba(NO_3)_2$ solution. A yellow precipitate of $BaCrO_4$ indicates the presence of Cl^- in the unknown substance.

*(110) **Cyanide.**—Dissolve a little of the original substance in water or in cold dilute HCl. Add a few drops each of $FeSO_4$ and $Fe_2(SO_4)_3$ solutions, and then NaOH solution to alkaline reaction. Boil for a short time, and acidify with HCl. A precipitate of Prussian blue, $Fe_4(Fe(CN)_6)_3$, indicates the presence of CN^- in the original substance.

Note.—A blue precipitate formed on adding the Fe solutions indicates the presence of $Fe(CN)_6^{----}$ or $Fe(CN)_6^{---}$. For the proper technique in this complication, see advanced texts.

*(111) **Thiocyanate and Ferrocyanide.**—Acidify a small portion of the solution with HCl and add a few drops of $FeCl_3$ solution. A red coloration, due to $Fe(SCN)_3$, indicates the presence of SCN^-[1]; a blue precipitate of Prussian blue, $Fe_4(Fe(CN)_6)_3$, indicates the presence of $Fe(CN)_6^{----}$.

[1] See (46, 4 and note).

Note.—The presence of colored cations like Cu, Co, etc. interferes with these tests by more or less masking the color changes. It is better to make these tests on the solution from which the "heavy metals" have been removed. (See (**117**), page 98.)

*(**112**) **Ferricyanide.**—Acidify a small portion of the solution of the unknown substance with HCl and add a few drops of $FeSO_4$ solution. A precipitate of $Fe_3(Fe(CN)_6)_2$ (Turnbull's blue) indicates the presence of $Fe(CN)_6^{----}$.

(**113**) **Sulfide.**—Place a small portion of the original substance, finely powdered (if a solid), in a beaker and add dilute HCl. Cover the beaker with a filter paper which has been moistened with 1 or 2 drops of $Pb(C_2H_3O_2)_2$ solution. Warm, if necessary, to start the action. A brown coloration on the paper shows the substance to contain S^{--}.

If the test is negative, and the unknown is a solid, add a little zinc dust. This modification is necessary to detect S^{--} in sulfides insoluble in HCl.

Test for Free Sulfur.—Place a little of the substance on a crucible lid and try to set fire to it with a Bunsen flame. A blue flame and the characteristic odor of SO_2 indicate the presence of sulfur. A still better test is to place a little of the substance in contact with a bright silver coin in a small beaker or dish, and warm with dilute NaOH solution. The formation of a black stain on the coin indicates free sulfur.

Note.—The action of acids on solids sometimes results in the separation of sulfur, usually discolored by the presence of small amounts of metallic sulfides. Probably the commonest source is the reaction between sulfides and HNO_3. Sulfur has a more or less distinctive behavior, in that it tends to float on the surface of the hot HNO_3 solution, buoyed up by bubbles of NO.

Group II

(**114**) **Nitrite.**—Acidify a portion of the original solution with a few drops of dilute H_2SO_4 and add $FeSO_4$ solution. A brown color, due to $FeSO_4.NO$, indicates the presence of NO_2^-.

Note.—See (**127,** 3), page 104, on the interference of nitrites with the test for nitrates.

(**115**) **Acetate.**—Place 3 or 4 cc. of concentrated H_2SO_4-alcohol mixture (side shelf) in a test tube, add a few drops

of the original solution and warm. The more or less pleasant ethereal odor of ethyl acetate, $C_2H_5C_2H_3O_2$, indicates the presence of $C_2H_3O_2^-$.

In case of doubt, place small amounts of the H_2SO_4-alcohol mixture in two test tubes. To one add 1 or 2 drops of $NaC_2H_3O_2$ solution and warm both tubes. Match the odor of the "unknown" with these two "knowns."

Note.—The test in which the acetate was added is known as a "control" test; the one without the acetate is known as a "blank" test. If acetate was found in the unknown, the test is said to be "positive;" if not found, "negative." This method of matching a doubtful test against "control" and "blank" tests is a general one, and may be applied in numerous other cases where there is doubt as to whether the test is positive or negative.

(116) Hydroxide and Oxide.—As stated in (89, 2), the tests for OH^- in a solution may be without significance on account of the phenomenon of hydrolysis. The presence of hydroxide or oxide in a solid substance can be established only indirectly. If no other anions can be detected in a substance, and the substance is evidently not an element, it may be suspected that the compound is either an oxide or a hydroxide. Such an inference should be confirmed by comparing the unknown substance with a known substance. They should be identical in such general properties as color, solubility, etc. In the case of mixtures, containing two or more anions, a *quantitative* analysis may be necessary to prove the existence of hydroxide and oxide.

Hydroxides may usually be distinguished from oxides by heating a small portion of the dry substance in a hard glass test tube held horizontally. A film of moisture forming on the cold part of the tube indicates hydroxide. Sodium hydroxide, NaOH, and potassium hydroxide, KOH, are not broken down by heat in this way, and do not give positive tests.

Group III

(117) Removal of Cation Groups I, II, III, and IV.—To a portion of the solution add excess of concentrated Na_2CO_3 solution and boil gently for 2 or 3 minutes in a covered beaker. Filter into a beaker, and reject the precipitate. Neutralize the

filtrate by excess of dilute HNO_3 (litmus test), boil, and reserve for (**118**, second paragraph).

Note.—Arsenic, on account of the acidic property of its oxides, is not removed by this process, but is present in the filtrate as AsO_3^{---} and AsO_4^{---}. Chromium may also be present as CrO_4^{--}, and manganese as MnO_4^{-}.

(**118**) **Test for Group III.**—To the filtrate from (**106**) or (**130**) add dilute NH_4OH drop by drop until the solution is neutral to litmus paper. If the neutral point is exceeded, boil in an open vessel until the odor of NH_3 is no longer perceptible in the vapors. A precipitate indicates the presence of Group III.

If the solution is the HNO_3 solution from (**117**), add $AgNO_3$ solution in slight excess to precipitate Anion Group I, and, without filtering, $Ba(NO_3)_2$ solution to precipitate Group V. Warm and filter. Add a drop each of $AgNO_3$ and $Ba(NO_3)_2$ solutions to the filtrate to insure the complete removal of these anion groups. Reject both precipitates. Neutralize the filtrate by adding NH_4OH drop by drop (litmus test). If the neutral point is exceeded, boil out the excess NH_4OH. A precipitate indicates the presence of Group III.

In both the above paragraphs, the precipitate indicates the presence of the Group III anions which form stable acids, *viz.*: $C_2O_4^{--}$, $C_4H_4O_6^{--}$, BO_3^{---}, AsO_3^{---}, AsO_4^{---}, PO_4^{---}, and CrO_4^{--}. If no precipitate forms, test portions of the original for the anions which form unstable acids, *viz.*: CO_3^{--}, SO_3^{--}, $S_2O_3^{--}$.

Notes.—1. $AgBO_2$ dissolves very readily in NH_4^+ salt solutions. Consequently, it may not be precipitated from the filtrate from (**106**), especially if BO_3^{---} were present in the original as free boric acid. The test on the filtrate from (**130**) is much more reliable.

2. The test on the filtrate from (**130**) may be vitiated in the presence of F^- by the formation of a precipitate of BaF_2 upon neutralization with NH_4OH. BaF_2 is fairly soluble in HNO_3, and is reprecipitated upon neutralization by a base.

(**119**) **Carbonate.**—Place a portion of the original substance in the test tube generator used in (**90**, 2). If the substance is a solid, it should be powdered, and enough water should be introduced to cover the end of the thistle tube. Add dilute H_2SO_4, heat to boiling, if necessary, and pass the gas given off through $Ca(OH)_2$ solution in a test tube. A white precipitate indicates

the presence of CO_3^{--} in the unknown substance. Reserve the solution in the generator for (**120.**)

Notes.—1. In the case of substances which effervesce freely, the CO_2 may be detected in an easier way than the above by holding a drop of $Ca(OH)_2$ solution on a piece of glass tubing above the surface of the liquid in the test tube. A white film, $CaCO_3$, indicates the presence of CO_3^{--}.

2. Native carbonates, like dolomite and siderite, react so slowly that the apparatus in Fig. 8 is necessary to give a satisfactory test.

3. In the case of the carbonates of Pb^{++}, Ba^{++}, etc., which form insoluble sulfates, dilute HNO_3 should be used instead of H_2SO_4. The insoluble sulfate forms a protecting film around the carbonate, which interferes with the action. When HNO_3 is used, excessive boiling should be avoided, since enough of the acid may be distilled over to neutralize completely the $Ca(OH)_2$.

4. Sulfites and thiosulfates, when present in very large quantity, may interfere with the test for carbonate in two ways: (*a*) In a mixture of carbonate and sulfite (or thiosulfate) the CO_2 is liberated first, and, after it is displaced, SO_2 begins to be evolved. However, since the CO_2 is first to reach the $Ca(OH)_2$ solution, a white precipitate of $CaCO_3$ is formed more or less temporarily, and then is redissolved by the SO_2, thus: $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$. This temporary precipitation strongly indicates the presence of CO_3^{--}. (*b*) In the presence of sulfite (or thiosulfate) and in the absence of carbonate, sufficient SO_2 may be formed to give a precipitate of the somewhat insoluble white $CaSO_3$, which might be mistaken for $CaCO_3$. The complication in both cases may be avoided by introducing a slight excess of $KMnO_4$ solution into the solution before adding the acid. The permanganate will oxide all SO_2 to H_2SO_4, which will be retained by the solution, while the CO_2 will pass over into the lime water. See advanced textbooks for the technique for the detection of carbonates and oxalates in the presence of sulfites, thiosulfates, etc.

(**120**) **Oxalate.**—Use an acidified solution of the original substance from which the carbonate has been expelled, as the solution from (**119**). To make sure that all the carbonate has been expelled, the solution should be boiled in an open dish for about a minute. Place a little pure MnO_2 in the test tube generator outfit used in (**90**, 2), add the solution, warm gently, and test any gas evolved for CO_2 by bubbling it through $Ca(OH)_2$ solution. A white precipitate indicates the presence of $C_2O_4^{--}$ in the original substance.

*(**121**) **Tartrate.**—Heat a little of the dry substance in a porcelain crucible or on a crucible lid. A charring effect, with an odor suggesting "burned sugar," indicates the presence of organic

substances, and tartrates may be present. If the material does not char, tartrates are absent.

If tartrates may be present, remove Cation Groups I, II, III, and IV by (**117**). Neutralize the free HNO_3 with NH_4OH, and heat to boiling to expel the excess NH_4OH. Add $CaCl_2$ solution in excess and allow the mixture to stand for a short time.[1] If a precipitate forms, filter, and digest it cold in NaOH solution. Dilute slightly, filter, and boil the filtrate. If a precipitate forms, $C_4H_4O_6^{--}$ is indicated. Filter hot, wash with a little warm water, and transfer the precipitate to a test tube. Add 1 drop of NH_4OH and a little $AgNO_3$ solution and warm. If $C_4H_4O_6^{--}$ is present, it will reduce the $AgNO_3$ to metallic silver, which will appear as a black precipitate or a silver mirror on the walls of the test tube.

(**122**) **Sulfite and Thiosulfate.**—Place a little of the original substance in the test tube generator outfit described in (**90**, 2) and add dilute H_2SO_4. Warm gently and pass any gas evolved through some dilute $BaCl_2$ solution to which has been added a drop of $KMnO_4$ solution. The bleaching of the purple color and the formation of a white precipitate of $BaSO_4$ indicate that the gas evolved was SO_2. A creamy precipitate of free sulfur in the generator tube indicates $S_2O_3^{--}$; the absence of free sulfur indicates SO_3^{--}.

Notes.—1. $KMnO_4$ oxidizes SO_2 to SO_4^{--}, which combines with the Ba^{++} of the $BaCl_2$ to form insoluble $BaSO_4$.

2. See advanced textbooks for the detection of SO_3^{--} and $S_2O_3^{--}$ in the presence of each other.

3. Sulfites are easily oxidized to sulfates, so that commercial sulfites always contain a little sulfate, due to atmospheric oxidation.

(**123**) **Arsenite and Arsenate.**—Although As is always found in the cation analysis, it may have been present in the original substance in the anion group. If, in the absence of Anion Group I, and barring interferences with other members of Anion Group III, a neutral solution gives with $AgNO_3$ a chocolate brown precipitate, AsO_4^{---} is indicated; if the precipitate is yellow, AsO_3^{---} is indicated.

[1] Rubbing the inside wall of the test tube with a stirring rod may hasten the formation of the precipitate.

Note.—Arsenic occurs in the cation form in the following cases only: In *acid* solutions, as As^{+++} in $AsCl_3$, $AsBr_3$, and AsI_3 (and perhaps some halogen-oxygen derivatives); in solids, as As^{+++} and As^{+++++} in oxides and sulfides, like As_2O_3, As_2O_5, As_2S_3 and As_2S_5. In all other compounds it is present in the anion groups, like AsO_4^{---}, AsO_3^{---}, AsS_4^{---}, etc.

(**124**) **Phosphate.**—If AsO_4^{---} has been found, it must be removed as follows: Acidify a portion of the solution of the substance with HCl, dilute to 40 cc., and then add 4 cc. more of dilute HCl. Heat to boiling, add 1 cc. of NH_4I solution, and saturate with H_2S. (See (**27**), page 24.) When the precipitation is complete, filter and reserve the filtrate for the next paragraph.

Remove chlorides from the solution by adding 5 cc. of concentrated HNO_3 and evaporating nearly to dryness. Take up the residue in a few cubic centimeters of dilute HNO_3 and proceed as follows: To the solution, now free from arsenates and chlorides (or other halides), add 5 cc. of *clear* ammonium molybdate solution, $(NH_4)_2MoO_4$, warm, and allow to stand. A yellow precipitate of the approximate composition $(NH_4)_3PO_4.12MoO_3$ indicates the presence of PO_4^{---}.

Notes.—1. Arsenates give with $(NH_4)_2MoO_4$ a yellow precipitate similar to the phosphate precipitate.

2. The purpose of the evaporation with HNO_3 is to remove Cl^- or other halide ions. The $(NH_4)_2MoO_4$ test for PO_4^{---} is not sensitive in the presence of halide ions.

(**125**) **Borate.**—Dissolve a little of the substance in HCl, dip a piece of turmeric paper (storeroom) in the solution, and dry it by placing it on a watch glass above a beaker of boiling water. A red color indicates the presence of a borate. The test should be further confirmed by touching the paper with a drop of NaOH solution on a stirring rod, which gives an olive-green tint in the presence of BO_3^{---}.

Note.—The presence of free H_2SO_4 vitiates this test. Upon evaporation, the acid is concentrated and chars the paper. If H_2SO_4 is present, add $BaCl_2$ solution in slight excess to precipitate the SO_4^{--}, and then proceed as above.

Alternate Test.—Place a little of the solid substance (obtained if necessary by evaporating the solution, first made alkaline with NaOH, since H_3BO_3 is volatile in steam) in a small porcelain

dish, and add about 5 cc. of alcohol-concentrated H_2SO_4 mixture (side shelf). Warm the dish and set fire to the vapors. If a borate is present, gaseous ethyl borate, $(C_2H_5)_3BO_3$, is formed, which burns with a green flame.

Note.—This test is not reliable in the presence of Cu^{++} or Ba^{++}. Cl^- may also interfere by forming ethyl chloride, C_2H_5Cl, which tinges the flame green.

(126) Chromate and Dichromate.—The presence of these ions is indicated during the cation analysis by the change of color from orange to milky-green during the H_2S precipitation of Group II (see (**27**), page 24) and by the subsequent detection of Cr^{+++} in (**53**) of Group III.

In case of doubt, acidify a portion of the unknown solution with a few drops of dilute HNO_3, add 1 or 2 cc. of ether and a few drops of H_2O_2 solution, and shake. A blue color in the ether layer indicates the presence of CrO_4^{--} or $Cr_2O_7^{--}$. (See (**53**), page 48.)

Notes.—1. The presence of Cl^- or other halide ion interferes with the H_2O_2 test.

2. Chromates and dichromates usually may be distinguished by the color of their water solutions, chromates being yellow and dichromates orange-red. (Exceptions are $CuCrO_4$ and $Cr_2(CrO_4)_3$, which give brown solutions.) Acid solutions can contain only $Cr_2O_7^{--}$ and neutral or alkaline solutions only CrO_4^{--}. In the solid state the colors are not so uniform. Solid chromates are usually yellow, though Ag_2CrO_4 and $HgCrO_4$ are red, and $CuCrO_4$ is brown. There are only a few solid dichromates, and their color is generally orange-red, though $(BiO)_2Cr_2O_7$ is yellow.

Group IV

(127) Nitrate.—To a small portion of the unknown solution in a test tube add an equal volume of concentrated $FeSO_4$ solution, and by means of a thistle tube (see (**99**, 2)) introduce concentrated H_2SO_4 below the mixture. A brown ring at the junction of the two layers indicates the presence of NO_3^- in the solution.

Notes.—1. The brown $FeSO_4.NO$ is decomposed by heat. Consequently, the test must be made on cold solutions.

2. Chlorates, chromates, and iodides interfere with this test. Advanced texts may be consulted as to their removal.

3. Nitrites give a brown color with $FeSO_4$ solution before the H_2SO_4 is added. There is no perfectly satisfactory way for testing for NO_3^- in the presence of NO_2^-, since in the removal of the latter some NO_3^- is always formed.

*(**128**) **Chlorate.**—Add a few drops of concentrated H_2SO_4 to a *very small* portion of the solid substance in a test tube. The formation of the greenish-yellow gas, ClO_2, which colors the H_2SO_4 yellow, and explodes violently on heating, indicates the presence of ClO_3^-. *During the test be careful not to hold the face over the tube, or to point the tube at any one.*

Note.—Iodides, nitrates, and chromates interfere with this test by forming yellow solutions. For the procedure in such cases consult advanced textbooks.

(**129**) **Permanganate.**—The permanganate ion, MnO_4^-, is detected during the analysis for cations. A red-to-violet solution, decolorized during the H_2S precipitation in (**27**), and the detection of Mn^{++} in (**55**) are sufficient indications of the presence of this ion.

Group V

(**130**) **Test for Group V.**—Acidify a solution of the substance with a small excess of dilute HNO_3, add $Ba(NO_3)_2$ solution until precipitation is complete, dilute with an equal volume of water, and warm. A precipitate indicates the presence of the anions of Group V. Filter and reserve filtrate for (**118**).

(**131**) **Sulfate.**—Acidify a small portion of the original solution with 1 cc. of concentrated HNO_3 and add $Ba(NO_3)_2$ solution slowly until precipitation is complete. Now add an equal volume of water and warm. A white precipitate indicates the presence of SO_4^{--}. Filter and reserve the filtrate for (**132,** 1).

Notes.—1. The insolubility of the precipitate in warm water distinguishes the insoluble $BaSO_4$ from the moderately soluble $Ba(NO_3)_2$. See (**102,** 2, note).

2. $Ba(NO_3)_2$ solution is preferred to $BaCl_2$ solution as a reagent for SO_4^{--}, because the Cl^- ion of the latter combines with certain cations, forming insoluble chlorides which might be mistaken for $BaSO_4$. See (**102,** 1, note).

*(**132**) **Fluoride.**—(*a*). The substance is a solution. Add a little $CaCl_2$ solution. If, upon standing, a white slimy precipitate appears, warm and shake. Filter, and drain the precipitate as

thoroughly as possible, and dry by heating on a watch glass over a beaker of boiling water. Test the residue for fluoride by the following paragraph.

(*b*). The substance is a solid. Place a little of the solid (in the form of a powder) in a dry test tube, moisten with 2 or 3 drops of water, and add 2 or 3 cc. of concentrated H_2SO_4. Warm gently and hold just above the liquid in the test tube a glass tube carrying a drop of water. A turbidity in the drop indicates the presence of F^-.

Notes.—1. Precipitated CaF_2 is gelatinous and filters very slowly.

2. The acid is slightly diluted, since 90 per cent H_2SO_4 gives a better reaction with CaF_2 than the ordinary concentrated H_2SO_4 (about 96 per cent).

Group VI

*(**133**) **Silicate.**—If the unknown substance is in solution, place a small portion in a Pyrex beaker, and add dilute HCl drop by drop until the mixture is decidedly acid. Evaporate just to dryness, taking care not to overheat. Moisten the residue with concentrated HCl and add hot water. The insoluble residue is SiO_2. Filter, wash the precipitate, and test it by the next paragraph.

If the unknown substance is a solid (either the residue from the preceding paragraph, or a substance insoluble in acids), powder it thoroughly, and try its solubility in Na_2CO_3 and $NaPO_3$ beads. Silica or a silicate will dissolve in the carbonate with effervescence, but will be insoluble in the metaphosphate bead, forming a "silica skeleton."

Exercises

1. List the acids too volatile to be found in strongly acid solutions open to the air.
2. List the acids too unstable to be found in strongly acid solutions.
3. A solid, insoluble in water, but soluble in HNO_3, contains Pb^{++}. What anions may be present?
4. A strongly acid solution contains Ag^+ and Ba^{++}. What anions may be present?
5. What anions might be present in a neutral solution containing Cd^{++} and Sr^{++}?
6. An unknown, insoluble in water, but soluble in dilute HCl, contains Mn^{++} and Zn^{++}. What anions would one test for? If the unknown

dissolved in HCl without effervescence, which of these anions could not be present?

7. An acidic solution containing Cu^{++} as its only metallic ion can be neutralized without precipitate formation. What anions might be present?
8. What cations could be present in a neutral solution containing PO_4^{---}? CrO_4^{--}?
9. A neutral solution is found to contain both Pb^{++} and SO_4^{--}. How is this possible when $PbSO_4$ is insoluble in water?
10. Name neutral salt solutions that will dissolve the following: (*a*) AgCl, (*b*) NiC_2O_4, (*c*) $Cu(OH)_2$, (*d*) $Mg(OH)_2$.
11. A white powder, insoluble in water, dissolves in dilute HCl without effervescence. Ca^{++} is the only cation found in the solution. List the possible calcium compounds.
12. A red ferric compound is insoluble in water, but dissolves in HCl to an amber solution. Tests for all the anions forming acid-soluble compounds with Fe^{+++} give negative results. What is the substance?
13. What two volatile acidic anhydrides are found, under special conditions, in industrial solutions having a definitely acid reaction?
14. What anions could not be present in a solid wholly insoluble in water?
15. What is the test for Cl^- in the absence of Br^- and I^-?
16. How could AgCl be separated from a mixture of Ag_2S and AgCl?
17. Name an oxidizing agent that will oxidize HI, but not HBr or HCl.
18. How would S^{--} be tested for in HgS?
19. A white powder effervesces violently when concentrated H_2SO_4 is added. It dissolves readily in water, giving a solution which forms a brown precipitate with $AgNO_3$ solution. Analysis gives a strong test for Na^+ and a weak test for CO_3^{--}, all other tests being negative. What is the powder?
20. Cation analysis of an unknown solution indicates Pb^{++} and NH_4^+. $C_2H_3O_2^-$ is indicated as present as an anion by the H_2SO_4 test. What other anions should be tested for?
21. What procedure would be used in testing for the anions present in a solid, partially soluble in water, completely soluble in HNO_3, containing the cations Na^+ and Zn^{++}?
22. An unknown is in the form of an amber-colored solution containing a brown sediment. The solution does not give a yellow color to methyl violet. The only ions found in the analysis are Fe^{+++} and SO_4^{--}. Interpret.
23. Why should $S_2O_3^{--}$ be removed before testing for the presence of Anion Group I?
24. Why should commercial Na_2CO_3 contain small amounts of NaCl?
25. The presence of the Cation Groups I, II, III, and IV (sometimes called the "heavy metals") interfere with the tests for what group of anions?
26. Will boiling with concentrated Na_2CO_3 solution precipitate As from an unknown? In an alkaline solution, does As act as a metal or a non-metal?

27. Cation analysis of the solution of a simple salt shows the presence of K^+ and either As^{III} or As^{V}. The solution gives a yellow precipitate with $AgNO_3$ solution. Identify the salt.

28. Why should pure $NiSO_4$ appear to give the "brown ring" test for NO_3^-?

29. A yellow mercury compound is insoluble in water, but soluble in acids. The HCl solution of this substance gives negative tests for all anions except Cl^-, and the HNO_3 solution gives negative tests for all anions except NO_3^-. What is the substance?

30. What carbonates react with least vigor with acids?

31. How could you distinguish between pulverized CaF_2 and fine SiO_2 by use of the bead test?

PART III

SYSTEMATIC ANALYSIS

Note.—The following outline for the systematic analysis of unknown substances is not exhaustive, giving only methods for detecting the commoner elements in rather simple modes of combination. For a thorough treatment consult advanced textbooks.

In carrying out a complete analysis of an unknown substance, the student should take advantage of the information afforded by such properties as color, general appearance, solubility, behavior on solution, etc. If the material is a natural or commercial product, he should keep in mind the probable composition, should know what impurities are most likely, and should not waste any time testing for ions that common sense would indicate to be absent. As illustrative of this last point, a commercial alloy would not be likely to contain strontium or potassium, nor would an ore contain acetate or oxalate.

Proper attention should also be paid to the relative amounts of the various ingredients found. If only a trace of an ion is present, it should be reported as such. Due consideration should be given to the intensity of the test, since certain tests are much more sensitive than others. For example, a trace of Fe^{+++} gives a strong coloration with NH_4SCN solution.

REMOVAL OF ORGANIC MATTER

(**134**) Organic matter, if present, must be removed before carrying out the analysis for metallic ions. Hydroxy-organic compounds, like tartrates, citrates, sugars, etc., are particularly objectionable, since they prevent the precipitation of $Al(OH)_3$ and $Cr(OH)_3$ in Group III.

Test.—Heat a small portion of the solid substance (obtained in case of solutions by evaporation) in a porcelain crucible or

on a crucible lid. A charring effect and an odor like that of "burned sugar" indicate the presence of organic matter.

Removal.—If organic matter is present, place a larger portion of the substance in a small Pyrex beaker or flask, add 5 cc. of concentrated HNO_3 and 5 cc. of concentrated H_2SO_4, and evaporate until white fumes of SO_3 come off. If the solution is not colorless, or nearly so, add 5 cc. more of concentrated HNO_3, and evaporate again. This may be repeated as many times as necessary. Cool, dilute the solution, filter, and wash the precipitate. Analyze the solution for cations by (**14**) to (**78**). Test the residue for the cations forming insoluble sulfates by fusing a portion with Na_2CO_3 (page 114), for Al_2O_3 and Fe_2O_3 by fusing another portion with $KHSO_4$ (page 113), and for SiO_2, using a third portion, by (**133**). As usual, the test for NH_4^+ must be made on a portion of the original substance.

DISSOLVING THE SUBSTANCE

(**135**) **Solids, Not Metals or Alloys.**—The material, if not a metal or an alloy (see (**136**)), should be ground as finely as possible in a mortar, and then treated with the following solvents, both hot and cold, in the order given:

1. Water.
2. HNO_3, dilute and concentrated.
3. HCl, dilute and concentrated.
4. Aqua regia.

In case any one of the solvents effects a partial solution, the treatment should be continued as long as there is any action. The residue is then filtered off and subjected to the action of the other solvents or otherwise identified.

(**136**) **Metals and Alloys.**—There are certain natural limitations to the composition of alloys. With the exception of magnesium, the metals of Cation Groups IV and V are very seldom found in alloys that are stable towards water or ordinary (moist) air.[1] On the other hand, metals and alloys may contain certain non-metals, the most important of which are C, Si, and P, and are found in most iron alloys. Provisions for the detection of these substances are given in the procedure below.

[1] Certain bearing metals contain barium.

Dissolving the Material.—Use a small sample for analysis, not more than 0.5 gram. Preferably it should be in the form of filings, turnings, or pellets. Place the sample in a beaker, and add 10 cc. or more of dilute HNO_3. Cover with a watch glass, and heat over a low flame just below the boiling point of the acid, as long as brown fumes are given off. More acid may be added from time to time to replace that used up in the action or lost by evaporation.

The formation of a white precipitate (usually metastannic acid, $SnO_2.xH_2O$, or antimony oxide, Sb_2O_4) indicates that HNO_3 is not the proper solvent. In such a case add at once an equal volume of concentrated HCl, making aqua regia the solvent.

Note.—The adding of indefinite amounts of concentrated acids in order to effect a speedy solution of an alloy is discouraged. As will be seen below, excess of acid must be boiled out; moreover, in some cases, dilute acids are actually better solvents than concentrated acids.

If HNO_3 appears to have little effect on the substance, pour it off, wash the metal with a little water, and add 10 cc. of dilute HCl. Cover the beaker with a watch glass and warm. Certain metals and alloys, insoluble in HNO_3, dissolve freely in HCl; *e.g.*, Al, Fe, Cr, and their alloys.

Notes.—1. When metals, otherwise decidedly active, are inert towards HNO_3 and certain other oxidizing agents, they are said to be in the "passive state," a condition little understood. (See advanced textbooks.)

2. HCl, like HNO_3, has certain advantages and disadvantages as a solvent for alloys. While it reacts very rapidly with some metals, HCl, as a rule, is much slower than HNO_3, and is practically without action on metals occurring below hydrogen in the Electromotive Series. (See Appendix, page 126.) Furthermore, As and Sb, if present in small amounts, may be completely lost as arsine, AsH_3, and stibine, SbH_3, owing to the reducing action of the nascent hydrogen. The proper solvent for an unknown alloy must be determined experimentally.

If a metallic-looking residue remains, insoluble in HNO_3 and HCl taken separately, add about 10 cc. of dilute HCl and 5 cc. of dilute HNO_3, and warm in a covered beaker until the action is complete.

Combine all the solutions obtained in the above paragraphs, reserving any insoluble residue for the tests for C and Si. If a precipitate is formed when the HNO_3 and HCl (or aqua regia) solutions are mixed, Cation Group I is present. Filter and

wash the precipitate, and analyze it by (**15**) and (**16**). Analyze the filtrate for the ions of Groups II, III, and IV and Mg^{++} by (**26**) and the subsequent procedures, reserving a small portion for the P test below.

Phosphorus.—Test a small portion of the filtrate from the above procedure for PO_4^{---} by (**124**), page 102. If PO_4^{---} is found, the presence of P in the alloy is indicated.

The residue insoluble in acids probably consists of such substances as C, SiO_2, SiC, etc. Dry by heating on a watch glass over a beaker of boiling water, and test portions of it as follows:

Carbon.—Place about 1 gram of dry $KClO_3$ in a dry hard glass test tube, and heat until the salt is just melted. Drop into the melt a minute (Be careful not to use too much!) portion of the residue. Inflammation, with a harmless explosion, indicates the presence of carbon.

Silicon.—Test another portion of the residue for SiO_2 by a metaphosphate bead. See (**104,** 3), page 88.

(137) Ores[1] and Insoluble Salts.—The material is ground to a very fine powder in a mortar, and the following solvents should be tried in order:

Water.—Place about 1 gram of the powdered substance in a beaker and add about 10 cc. of water and heat to boiling. If the material dissolves completely, analyze the solution for cations and anions according to the procedures in Parts I and II.

Nitric Acid.—If the substance is not soluble in water, add, without filtering, 5 cc. of concentrated HNO_3. Warm as long as brown fumes are given off, adding more HNO_3 if the action becomes slow. If the action with HNO_3 appears incomplete, allow the heavy precipitate to settle and decant the solution

[1] An ore may be defined as a natural substance containing a given element in sufficient amount for it to be profitably extracted. Broadly speaking, rock salt (halite) is just as truly a sodium ore as chalcocite is a copper ore. It follows, then, that ores can range in solubility all the way from water-soluble to acid-insoluble. A metal may be present in the ore in the free or "native" state, or in combination with some negative group, most frequently sulfide, oxide, carbonate, or sulfate. In a strictly analogous sense, phosphorite, $Ca_3(PO_4)_2$, might be regarded as a phosphorus ore. The valuable ingredient is usually mixed with considerable amounts of rocky material, frequently siliceous, so that on dissolving many ores a residue of SiO_2 remains.

through a filter, and repeat the HNO_3 treatment on the residue. Filter, and reserve all filtrates for later analysis.

Aqua Regia.—If the residue from the HNO_3 treatment seems to consist of something more than silica, add 10 cc. of dilute HCl and 5 cc. of dilute HNO_3 and warm. When the reaction is complete, dilute and filter, reserving the residue for the next paragraph. Combine all the filtrates obtained up to this point. If a precipitate forms upon mixing the aqua regia solution with the HNO_3 solution, Cation Group I is present. Filter, wash the precipitate, and treat the residue by (**15**) and (**16**), and the filtrate[1] by (**26**) and the subsequent procedures.

Examine the residue closely. If the substance is an ore, the residue may be nothing but sand discolored by traces of the undissolved substance. Test it in a metaphosphate bead. (See (**104**, 3), page 88.) If the residue is gummy, and tends to float in the hot HNO_3 or aqua regia solution, it may be sulfur. Test it by (**113**). If the residue seems to have been practically unaffected by the acid treatment, and especially if the acid solution appears to contain very little dissolved material, a substance insoluble in acids is indicated. Proceed to the next paragraph.

Fusion with Potassium Hydrogen Sulfate.—Mix the substance insoluble in acids with 10 or 12 times its weight of solid potassium hydrogen sulfate (also called potassium bisulfate), $KHSO_4$, and grind them together in a clean mortar. Transfer the mixture to a porcelain crucible, and heat over a strong flame (a Meker burner (storeroom) or a blast lamp should be used), at first gently until frothing has ceased, and then at maximum heat until a clear melt is obtained. Allow the crucible to cool, place it on its side in a beaker, and cover with water containing 4 cc. of dilute HNO_3. As soon as the solid is detached from the crucible, remove the latter. By means of the rounded end of a stirring rod, carefully disintegrate any solids in the mixture. Boil gently for 5 minutes and filter. Wash the precipitate,[2]

[1] In case of doubt as to whether the solution contains any metallic ions, evaporate a small portion on a watch glass over a beaker of boiling water. If no residue remains, discard the solution.

[2] If the decomposition of the insoluble substance by the $K_2S_2O_7$ seems incomplete, repeat the fusion with a fresh charge of $KHSO_4$.

and reserve it for the next paragraph. Analyze the filtrate for cations according to (**14**) to (**78**).

Notes.—1. The residue insoluble in acids may contain S, AgCl, $PbSO_4$, $PbCrO_4$ (fused), SnO_2 (native), Al_2O_3 (ignited), Cr_2O_3 (ignited), $Fe(CrO_2)_2$, $BaSO_4$, $SrSO_4$, $CaSO_4$, CaF_2, SiO_2, and many silicates. Ag^+ is present as AgCl, since the previous aqua regia treatment converts AgBr, AgI, and AgCN into AgCl.

2. Upon heating, $KHSO_4$ first melts, and at about 300° decomposes, giving potassium pyrosulfate, thus: $2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$. At still higher temperatures further decomposition takes place, giving the normal sulfate and SO_3: $K_2S_2O_7 \rightarrow K_2SO_4 + SO_3$. The solvent action of $K_2S_2O_7$ is similar to that of H_2SO_4, but more intense, since it may be used at higher temperatures.

3. Fusion with $KHSO_4$ brings about the following changes: S is volatilized or oxidized; AgCl is converted into Ag_2SO_4, $PbCrO_4$ into $PbSO_4$ and $Cr_2(SO_4)_3$, Al_2O_3 into $Al_2(SO_4)_3$, Cr_2O_3 into $Cr_2(SO_4)_3$, CaF_2 into $CaSO_4$ and KF, and silicates are "opened up" so that their cations may be brought into solution by acids. The filtrate contains the cations which form soluble sulfates; and the residue contains the insoluble sulfates $PbSO_4$, $BaSO_4$, $SrSO_4$, and $CaSO_4$, along with other insoluble substances like SnO_2 and SiO_2.

Fusion with Sodium Carbonate.—Mix the residue not decomposed by the pyrosulfate fusion with 5 to 10 grams of anhydrous Na_2CO_3 (or better, $NaKCO_3$) and 1 gram of KNO_3 and heat in a porcelain[1] crucible over a Meker burner (storeroom) or blast lamp until the melt ceases to effervesce or show any signs of action. If the reaction seems incomplete, more Na_2CO_3 should be added and the mixture again heated. After the reaction is complete, cool, place the crucible in a Pyrex beaker, cover with water, and boil for some time. If some of the material adheres to the crucible, remove the latter from the beaker, and carefully loosen the melt by means of a stirring rod. Break up all large particles with a spatula or stirring rod, filter, and wash the residue. Reject the filtrate. Add to the residue 4 cc. of dilute HCl and 20 cc. of water and warm as long as any of the substance seems to dissolve. Filter, wash the pre-

[1] A platinum crucible, if available, is much more satisfactory, provided easily reducible metals like Ag, Pb, Bi, As, Sb, and Sn are absent. These metals form easily fusible alloys with Pt, with the result that the crucible is melted out and ruined. The chief difficulty in using porcelain is that this material is attacked by the alkaline melt, and certain amounts of Al and SiO_2 are introduced into the substance.

cipitate, and analyze the filtrate for cations by (**26**) to (**70**). Besides Pb^{++}, Ba^{++}, Sr^{++}, and Ca^{++}, other cations not completely removed by the pyrosulfate fusion may be detected.

The residue contains SnO_2 and probably some undecomposed silicates, sulfates, etc. If SnO_2 may be present, treat the residue according to the next paragraph.

Notes.—1. $NaKCO_3$ is preferred, since it fuses more readily than Na_2CO_3.

2. The KNO_3 is added to the fusion mixture to help transpose oxidizable substances like Cr_2O_3.

3. The filtrate from the Na_2CO_3 fusion may contain, besides Na_2SO_4, Na_2SiO_3, and Na_2CO_3, such soluble materials as Na_3AsO_4 and Na_2CrO_4. If As and Cr have not been detected already, and if they might be present in the original, this solution should be analyzed for AsO_4^{---} and CrO_4^{--} in the regular way.

Native Stannic Oxide (*Cassiterite*).—Mix a portion of the residue from the preceding paragraph with 6 times its weight of Na_2CO_3 and S (equal parts mixed together), cover the crucible with a crucible lid, and heat over a small flame until the excess of sulfur has distilled off and burned. The operation requires about 20 minutes. Allow the crucible to cool and then treat its contents with hot water. Filter out any undissolved residue and analyze the filtrate for Sn^{++++} by (**34**) and (**35**), page 30, or (**38**) to (**41**), page 32.

Note.—The reaction involved in this procedure is: $2SnO_2 + 2Na_2CO_3 + 9S \rightarrow 3SO_2 + 2Na_2SnS_3 + 2CO_2$. Iron and other metals that might be present remain in the residue as insoluble sulfides.

TABLE XVII.—SOLUTION OF SOLIDS INSOLUBLE IN ACIDS

Residue: S, AgCl, $PbSO_4$, fused $PbCrO_4$, native SnO_2, ignited Al_2O_3 and Cr_2O_3, $Fe(CrO_2)_2$, $BaSO_4$, $SrSO_4$, $CaSO_4$, CaF_2, SiO_2, and many silicates. Add $KHSO_4$, grind in a mortar, fuse in porcelain crucible, cool and extract with hot dilute HNO_3.

Solution: All cations except Pb^{++}, Ba^{++}, Sr^{++}. Analyze solution by (**14**) to (**78**).

Residue: $PbSO_4$, $BaSO_4$, $SrSO_4$ $CaSO_4$, SnO_2, SiO_2 (and some of the acid-insoluble residue not decomposed in the pyrosulfate fusion). Mix with Na_2CO_3 (or $NaKCO_3$) and KNO_3 and fuse in porcelain crucible. Disintegrate residue, extract with hot water. Filter, wash precipitate.

Filtrate: Na_2SO_4, Na_2SiO_3, Na_2CO_3. Discard.

Residue: $PbCO_3$, $BaCO_3$, $SrCO_3$, $CaCO_3$, SnO_2 (and some unchanged sulfates and silicates). Extract with hot dilute HNO_3. Wash residue.

Solution: Pb^{++}, Ba^{++}, Sr^{++}, Ca^{++}. Analyze by (**26**) to (**70**).

Residue: SnO_2 and undecomposed sulfates, silicates, etc. Make special test for native SnO_2.

APPENDIX

THE LABORATORY RECORD

A complete record of all laboratory exercises should be kept in one of the official notebooks prescribed for the course.

Preliminary Experiments.—The notes on the preliminary experiments should contain in outline form a record of all the processes carried out, along with a clear statement of the results obtained and the inferences drawn. The style should be concise, rather than narrative and descriptive. As far as possible, the device of "labeled equations" should be used. By way of example, specimen notes on the preliminary experiments on the silver ion, Ag^+, are given below.

Specimen Notes

(12) Silver, $Ag.^+$ March 10, 1924.

1. *Insolubility of Silver Chloride in Water.*

$$AgNO_3 + HCl \rightarrow \underline{AgCl} + HNO_3.$$

Silver-chloride white, curdy, washed by decantation.

AgCl is insoluble in water, because washings with hot water gave no brown precipitate with H_2S.

2. *The Silver-ammonia Complex.*

$$\underline{AgCl} + 2NH_3 \rightarrow Ag(NH_3)_2Cl.$$

Silver-ammonia chloride colorless.

$$Ag(NH_3)_2Cl + 2HNO_3 \rightarrow \underline{AgCl} + 2NH_4Cl.$$

It will be noted that equations alone are not sufficient. Descriptive and interpretative statements must be included when called for in the laboratory directions.

Underscore all precipitates; gases formed should be indicated by overscoring or by arrows pointed upward. Solutions are designated by omitting these signs. See above specimen notes.

The headings of the experiments should always be included in the notes, since they indicate not only the subject, but frequently the inferences reached in the experiments.

Equations should show only the substances which are actually used or formed in the reaction. If a reaction takes place "in the presence of" a substance, indicate the latter by placing its formula above the arrow, thus:

$$Cu(NO_3)_2 + H_2S \xrightarrow{\text{Dil. HCl}} \underline{CuS} + 2HNO_3.$$

Do not write an equation every time two substances are mixed. For example, $Cu(NO_3)_2$ solution and dilute HCl may be assumed to mix without change. Be able to give evidence of a chemical change for every equation written.

The first time a new substance is encountered its name should be given and its properties described. Thereafter merely indicate whether it is a gas, solution, or precipitate by the convention described above.

Record of Unknowns.—Many forms have been devised for recording the results of the analyses on unknown substances. The following is recommended not only as convenient, but as providing a systematic arrangement of results and requiring only a small amount of the time of the student:

SPECIMEN NOTES ON THE ANALYSIS OF AN UNKNOWN

Unknown No. 9. Analysis begun: Oct. 1.
Serial Number: 641. Analysis Completed: Oct. 3.
Nature of Unknown: Yellow alloy. Date Due: Oct. 5.
Solvent: Warm dilute HNO_3, giving green solution.

No.	Substance	Treatment	Result	Inference
1	Alloy	Dilute HNO_3	Green solution	Cu (?)
2	Solution #1	Evaporation	Green residue	
3	Residue #2	4 cc. HCl, H_2O	Solution	No Ag
4	Solution #3	H_2S	Dark precipitate	
5	Precipitate #4	$(NH_4)_2S_2$	Dark residue	Cu subgroup
6	Residue #5	Dilute HNO_3	Solution, S residue	No Hg
7	Solution #6	H_2SO_4, evaporate, dilute	Slight white precipitate	Pb (?)
8	Precipitate #7	$NH_4C_2H_3O_2$	Solution	
9	Solution #8	$K_2Cr_2O_7$, $HC_2H_3O_2$	Slight yellow precipitate	Pb (trace)?
10	Filtrate #7	NH_4OH	Deep blue solution	Cu
11	Solution #10	H_2SO_4, Fe		
12	Filtrate #11	H_2S	No effect	No Cd
13	Filtrate #5	Sat. $H_2C_2O_4$	White precipitate	
14	Filtrate #13	HCl, Al, $HgCl_2$	No effect	No Sn
15	Residue #14	HNO_3, $NaKC_4H_4O_6$, Mag. mixt., NH_4OH	No effect	No As
16	Solution #15	H_2S	No effect	No Sb
17	Filtrate #4	NH_4OH, H_2S	White precipitate	Al or Zn
18	Precipitate #17	Dil. HCl	Colorless solution	No Ni or Co
19	Solution #18	NaOH, Na_2O_2	Colorless solution	No Fe subgr.
20	Solution #19	HNO_3, NH_4OH	No effect	No Al
21	Solution #20	Divide		
22	Solution #21	HNO_3, H_2O_2, ether	No effect	No Cr
23	Solution #21	$HC_2H_3O_2$, $K_4Fe(CN)_6$	White precipitate	Zn
24	Solution #17	$(NH_4)_2CO_3$	No effect	No Gr. IV
25	Solution #24	Na_2HPO_4	No effect	No Mg

Reported: Cu, Zn Alloy = Brass (with lead).
Present: Pb (trace), Cu, Zn.
Remarks: Pb was not reported because the precipitates in reactions 7 and 9 looked too small to be considered dependable tests.
Grade.....

.....
Instructor's Signature

Note.—The number in the second column of the table refers to the line in which the substance was formed; *e.g.*, filtrate #4 in line 17 means the filtrate from the precipitation by H_2S, as mentioned in line 4; it does not mean the fourth filtrate in the analysis.

After an analysis has been reported, the student should discuss with his instructor any mistakes, and enter, under the heading "Remarks," explanation of the errors in the procedure that caused the erroneous inferences. These reports must be graded or viséed by the instructor before other unknowns will be issued to the student.

UNKNOWNS

Issuing Unknowns.—Substances for analysis are obtained at the storeroom on cards furnished by the instructor. The following is suggested as a very convenient form of card for this purpose:

QUALITATIVE ANALYSIS REPORT CARD

Name..... Unknown No.....
Desk..... Serial No.....
Date Issued..... Grade.....
Date Reported.....

	Group I	Group II	Group III	Group IV	Group V	
Cations						
Anions						Group VI

Instructor's Signature.....

It is recommended that, before issuing the card for the unknown, the instructor give the student a brief oral quiz, so as to be sure the latter is ready to begin the analysis, and that he has an adequate understanding of how to proceed. The instructor should fill in the date and the series or group of unknowns, and should sign his name (or initials). The storekeeper will enter the serial number of the unknown issued and on his own record

both the serial number[1] and the corresponding code number. A very satisfactory code for unknowns consists of a number or a letter to indicate the series or group of unknowns (corresponding to "Unknown No. ....." on the card) and a second number showing the number of the unknown in that series; for example, I-6 or D-14. The entries in the storekeeper's record will then be of the following type:

643—I-6,
644—III-2,
645—V-14, etc.

The code numbers for unknowns must never be told to students, and the storekeeper's records should be carefully kept from spying.

When the student has finished his analysis he will enter in the proper squares the ions found, and turn the card in at the storeroom. The instructor will later grade the analysis, and the card will be filed as a permanent record in the storeroom.

Compounding Unknowns.—Unknowns, especially for beginners, should be relatively simple substances, and the ingredients should be mixed in approximately equal parts. Liquid unknowns should be made from very concentrated solutions, so that a 4-cc. sample (see page 5) will be sufficient for an analysis. These liquid unknowns are most conveniently dispensed from 1000-cc. bottles (cylindrical form), fitted with a one-hole rubber stopper carrying a short piece of glass tubing to serve as a delivery spout (see Fig. 11). The liquid is discharged through the tube in the familiar "hair tonic" fashion.

FIG. 11.—Bottle for unknown solutions and side-shelf reagents.

Solids should be thoroughly mixed and stored in 500-cc. salt-mouth bottles. Samples for analysis may be conveniently issued in small paste-board boxes ("pill boxes"), a reasonably large number of which should be kept on hand filled, ready for issuing. Proper care must be taken to prevent mixing of the boxes containing the different unknowns. These boxes should be unmarked—at least they should show nothing more than the class number or letter.

A considerable amount of chemical discretion and good judgment should be used in making up unknowns. In the case of solutions, care must be taken that the ingredients cannot react with each other so as to form precipitates (especially acid-insoluble precipitates), or to destroy one or more of the analytical ingredients. As a general rule, nitrates and acetates are most suitable, since these salts for most metals are uniformly soluble in water. Unfortunately, the nitrates and acetates of certain cations are hydrolytically decomposed. In the case of solids, not only must the above precautions be taken, but also the further one, that each ingredient, and each possible product by the metathetical action of ingredients, must not be deliquescent. Failure to observe this precaution will cause the caking of the solids in the

[1] For entering these serial numbers, the use of a numbering stamp, set for duplicate numbers, will be found very convenient.

stock bottle, and the disintegration of the pill box containers. The following are some of the combinations to be avoided:

Ag^+ salts with chlorides, bromides, iodides, etc.

Sulfates with salts of Pb^{++}, Ba^{++}, Sr^{++}, etc.

Ag^+, Hg^{++}, and Cu^{++} with reducing agents like Sn^{++}, SnO_2^{--}, SO_3^{--}, etc.

Chromates, dichromates, and permanganates with salts of oxidizable acids; for example, bromides, iodides, oxalates, sulfides, sulfites, etc.

Salts of unstable acids with salts which form acid solutions through hydrolysis; for example, Na_2CO_3 mixed with excess of $Al_2(SO_4)_3$ might, upon standing, fail to give a test for CO_3^{--}, owing to loss of CO_2.

Nitrites with iodides, and nitrites with NH_4^+ salts.

Fluoride solutions in glass containers.

Solutions of sulfides.

Strongly alkaline solutions in common glass bottles.

Chlorates with acid or oxidizable materials.

Metals and Alloys.—These materials are best issued in the form of borings, or as pellets formed by melting the material and pouring it into cold water.

TABLE OF SOLUBILITIES

	Acetate	Arsenate	Arsenite	Borate	Bromide	Carbonate	Chlorate	Chloride
Aluminium	Water	Acids	.....	Acids	Water	.....	Water	Water
Ammonium	Water	Water	Water	Water	Water	Water	Water	Water
Antimony	.....	.....	.....	.....	HBr	.....	.....	HCl
Arsenic	.....	.....	.....	.....	HBr	.....	.....	HCl
Barium	Water	Acids	Acids	Acids (2)	Water	Acids	Water	Water
Bismuth	Water	Acids	.....	Acids	HBr	Acids	Water	HCl
Cadmium	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Calcium	Water	Acids	Acids	(1)	Water	Acids	Water	Water
Chromium (ic)	Water	Acids	.....	Acids	Water	.....	Water	Water or Insol.
Cobalt	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Copper (cupric)	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Ferric	Cold Water	Acids	Acids	Acids	Water	.....	Water	Water
Ferrous	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Lead	Water	HNO_3	HNO_3	HNO_3	(1)	HNO_3	Water	Hot water
Magnesium	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Manganese	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Mercuric	Water	Acids	Acids	.....	Water	Acids	Water	Water
Mercurous	(1)	Acids	Acids	.....	HNO_3 Br_2	HNO_3	Water	HNO_3 Cl_2
Nickel	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Potassium	Water	Water	Water	Water	Water	Water	Water	Water
Silver	(1)	HNO_3	HNO_3	HNO_3	KCN	HNO_3	Water	NH_4OH KCN
Sodium	Water	Water	Water	Water	Water	Water	Water	Water
Stannic	Water	Acids	.....	.....	Water	.....	.....	Water
Stannous	Water	Acids	Acids	Acids	Water	.....	.....	Water
Strontium	Water	Acids	Acids	(1)	Water	Acids	Water	Water
Zinc	Water	Acids	Acids	Acids	Water	Acids	Water	Water

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved. (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

TABLE OF SOLUBILITIES (*Continued*)

	Chromate	Cyanide (6)	Ferricyanide	Ferrocyanide	Fluoride	Fluosilicate	Hydroxide
Aluminium	.....	.....	.....	.....	Water	Water	Acids Alks.
Ammonium	Water	Water	Water	Water	Water	Water (3)	Water
Antimony	.....	.....	.....	.....	(1)	.....	Acids Alks.
Arsenic	.....	.....	.....	.....	.....	.....	Acids Alks.
Barium	Acids	(1)	Water	Water	HNO_3	Acids	(1)
Bismuth	Acids	(3)	.....	.....	Acids	Water	Acids
Cadmium	.....	(1)	.....	.....	(1)	Water	Acids NH_4OH
Calcium	Water	Water	Water	(1)	Insol.	(1)	(1)
Chromium (ic)	Acids	.....	.....	.....	Water	Water	Acids
Cobalt	Acids	Acids	Insol.	Insol.	(1)	Water	Acids NH_4OH
Copper (cupric)	Water	.....	Insol.	Insol.	(1)	Water	Acids NH_4OH
Ferric	Water	.....	Water	Insol.	(1)	Water	Acids
Ferrous	.....	.....	Insol.	Insol.	(1)	Water	Acids
Lead	HNO_3	(1)	(1)	Insol.	(1)	Water	HNO_3 Alks.
Magnesium	Water	Water	Water	Water	Acids	Water	Acids (2)
Manganese	Acids	.....	Insol.	Acids	Acids	Water	Acids
Mercuric	Acids	Water	.....	.....	Water	Water	
Mercurous	Acids	.....	Acids	.....	Water	(1)	
Nickel	Acids	Hot acids	Insol.	Insol.	(1)	Water	Acids NH_4OH
Potassium	Water	Water	Water	Water	Water	(1)	Water
Silver	HNO_3	Conc. HNO_3	Insol.	Insol.	Water	Water	
Sodium	Water	Water	Water	Water	Water	(1)	Water
Stannic	.....	.....	.....	Insol.	.....	Water	Acids Alks.
Stannous	Acids	.....	.....	Insol.	.....	Water	Acids Alks.
Strontium	(1)	Water	Water	Water	Acids	Water	(1)
Zinc	Acids	Acids	Acids	Insol.	Acids	Water	Acids Alks. NH_4OH

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

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TABLE OF SOLUBILITIES (*Continued*)

	Iodide	Nitrate	Nitrite	Oxalate (6)	Oxide	Perchlorate	Permanganate	Phosphate
Aluminium	Water	Water	. . . .	Acids	Acids or Insol.	Water	Water	Acids
Ammonium	Water	Water	Water	Water	. . . . .	Water	Water	Water
Antimony	(3)	. . . . .	. . . . .	. . . . .	Acids Alks.			
Arsenic	Water	. . . . .	. . . . .	. . . . .	Acids Alks.			
Barium	Water	Water	Water	Acids	(1)	Water	Water	Acids
Bismuth	Acids	HNO_3	. . . . .	Acids	Acids	. . . . .	. . . . .	Acids
Cadmium	Water	Water	Water	Acids	Acids	Water	Water	Acids
Calcium	Water	Water	Water	Strong acids	(1)	Water	Water	Acids
Chromium (ic)	Water	Water	. . . . .	(1)	Acids or Insol.	Water	Water	Acids
Cobalt	Water	Water	Water	Acids	Acids	Water	Water	Acids
Copper (cupric)	. . . . .	Water	Water	Acids	Acids	Water	Water	Acids
Ferric	Water	. . . . .	Water	Acids	Acids	Water	Water	Acids
Ferrous	Water	Water	Water	Acids	Acids	. . . . .	. . . . .	Acids
Lead	(1)	Water	Water	HNO_3	Acids	Water	Water	HNO_3
Magnesium	Water	Water	Water	Water	Acids	Water	Water	Acids
Manganese	Water	Water	Water	Acids	Acids	Water	Water	Acids
Mercuric	Acids	Water	Water	Acids	Acids	Water	Water	Acids
Mercurous	HNO_3	HNO_3	. . . . .	HNO_3	HNO_3	Water	. . . . .	HNO_3
Nickel	Water	Water	Water	Acids	Acids	Water	Water	Acids
Potassium	Water	Water	Water	Water	. . . . .	(1)	Water	Water
Silver	KCN	Water	(1)	HNO_3	HNO_3	Water	Water	HNO_3
Sodium	Water	Water	Water	Water	. . . . .	Water	Water	Water
Stannic	(3)	. . . . .	. . . . .	Water	Acids Alks. Insol.	Water	Water	Acids
Stannous	Water	. . . . .	. . . . .	Acids	Acids Alks.	Water	. . . . .	Acids
Strontium	Water	Water	Water	Acids	(1)	Water	Water	Acids
Zinc	Water	Water	Water	Acids	Acids	Water	Water	Acids

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved; (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

TABLE OF SOLUBILITIES (*Continued*)

	Silicate (7)	Sulfate	Sulfide	Sulfite	Tartrate (6)	Thiocyanate	Thiosulphate (6)
Aluminium	Acids (5)	Water	(3)	Acids	Water	Water	Water
Ammonium	(3)	Water	Water	Water	Water	Water	Water
Antimony	.....	.....	Conc. acids	.....	Acids		
Arsenic	.....	.....	HNO_3 or Aqua Regia				
Barium	Acids (5)	Insol.	(3) (2)	Acids	Acids	Water	(1)
Bismuth	Acids (5)	H_2SO_4	HNO_3	.....	Acids		
Cadmium	Acids (5)	Water	Acids	Acids	(1)	(1)	Water
Calcium	Acids (5)	(1)	(3)	Acids	Acids	Water	Water
Chromium (ic)	Acids (5)	Water	(3)	.....	Water	Water	
Cobalt	Acids (5)	Water	HNO_3	Acids	Water	Water	Water
Copper (cupric)	Acids (5)	Water	HNO_3	Acids	Water	Acids	
Ferric	Acids (5)	Water	Acids	.....	Water	Water	
Ferrous	Acids (5)	Water	Acids	Acids	(1)	Water	Water
Lead	HNO_3 (5)	(4)	HNO_3	HNO_3	HNO_3	(1)	HNO_3 (5)
Magnesium	Acids (5)	Water	(3) (2)	Water	Water	Water	Water
Manganese	Acids (5)	Water	Acids	Acids	(1)	Water	Water
Mercuric	.....	H_2SO_4	Aqua Regia	Acids	Acids	(1)	
Mercurous	.....	(1)	Aqua Regia	.....	(1)	Acids	
Nickel	Acids (5)	Water	HNO_3	Acids	Acids	Water	Water
Potassium	Water	Water	Water	Water	Water	Water	Water
Silver	HNO_3 (5)	Water	Conc. HNO_3	HNO_3	HNO_3	HNO_3 (5)	HNO_3 (5)
Sodium	Water	Water	Water	Water	Water	Water	Water
Stannic	.....	H_2SO_4	Acids	.....	Water	Water	Water
Stannous	.....	H_2SO_4	Acids	Acids	Acids	Water	Water
Strontium	Acids (5)	Insol.	(3) (2)	Acids	Acids	Water	Water
Zinc	Acids (5)	Water	Acids	Acids	Acids	Water	Water

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

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THE ELECTROMOTIVE SERIES

In the following list the metals are arranging in the order of their decreasing "electrolytic solution tension;" that is, in the order of their decreasing tendency to pass from the metallic into the ionic condition. Potassium, with the greatest tension, is at the top of the list, and gold, with the smallest, is at the bottom. This order corresponds, in a rough way, to the reactivity of the metals. The less common metals are omitted.

Potassium	Lead
Sodium	*Hydrogen*
Magnesium	Copper
Aluminium	Arsenic
Manganese	Bismuth
Zinc	Antimony
Cadmium	Mercury
Iron	Silver
Cobalt	Platinum
Nickel	Gold
Tin	

This list has certain valuable applications in Qualitative Analysis:

1. Any metal will displace from solution (that is, from its ionic form) any metal coming below it in the list, *e.g.*, Fe will displace Cu, but not Cd.

2. Metals occurring above hydrogen will dissolve in non-oxidizing acids, like HCl or dilute H_2SO_4; metals occurring below hydrogen will require oxidizing solvents, like HNO_3, concentrated H_2SO_4, or aqua regia.

The student is referred to textbooks on General and Physical Chemistry for the electrochemical applications of this series.

REAGENTS

The following is a list of the reagents required for this course. In the case of solutions, the composition and mode of preparation is indicated.

Desk Reagents

Ammonium Hydroxide, 6M.—Dilute 400 cc. of the concentrated ammonia water of commerce (28 per cent NH_3, sp. gr. = 0.90) with 600 cc. of water.

Concentrated Hydrochloric Acid, 12M.—Use the concentrated c.p. acid of commerce (37 per cent HCl); sp. gr. = 1.19.

Dilute Hydrochloric Acid, 6M.—Dilute 500 cc. of concentrated HCl with 500 cc. of water; sp. gr. = 1.12.

Concentrated Nitric Acid, 16 M.—Use the concentrated c.p. HNO_3 of commerce (69 per cent HNO_3); sp. gr. = 1.42.

Dilute Nitric Acid, 6M.—Dilute 380 cc. of concentrated HNO_3 with 620 cc. of water; sp. gr. = 1.20.

Concentrated Sulfuric Acid, 18M.—Use the concentrated c.p. acid of commerce (95 per cent H_2SO_4); sp. gr. = 1.84.

Dilute Sulfuric Acid, 3M.—Pour 200 cc. of concentrated H_2SO_4 slowly into 1,000 cc. of water, stirring constantly; sp. gr. = 1.19.

Acetic Acid, 6M.—Dilute 350 cc. of glacial acetic acid with 650 cc. of water.

Ammonium Carbonate, 2M.—Dissolve 250 grams of solid $(NH_4)_2CO_3$ in 1 liter of 6M NH_4OH.

Ammonium Chloride, 2M.—Dissolve 107 grams of c.p. NH_4Cl in 1 liter of water.

Ammonium Oxalate, 0.3M.—Dissolve 40 grams of $(NH_4)_2C_2O_4.H_2O$ in 1 liter of warm water.

Ammonium Polysulfide, 3M.—Place 200 cc. of concentrated NH_4OH and 25 grams of sulfur (flowers) in a large bottle, and saturate the mixture with H_2S; then add 200 cc. of concentrated NH_4OH and dilute to 1 liter. Shake well and filter or decant.

Barium Chloride, 0.5M.—Dissolve 120 grams of $BaCl_2.2H_2O$ in 1 liter of warm water.

Lead Acetate, 0.3M.—Dissolve 114 grams of $Pb(C_2H_3O_2)_2.3H_2O$ in 1 liter of water. Filter, if necessary.

Potassium Dichromate, 0.3M.—Dissolve 90 grams of $K_2Cr_2O_7$ in 1 liter of hot water.

Potassium Ferrocyanide, 0.5M.—Dissolve 105 grams of $K_4Fe(CN)_6.3H_2O$ in 1 liter of water.

Silver Nitrate 0.3M.—Dissolve 51 grams of $AgNO_3$ in 1 liter of water.

Sodium Phosphate, 0.25M.—Dissolve 90 grams of $Na_2HPO_4.12H_2O$ in 1 liter of hot water.

Side Shelf

Liquids[1]

Alcohol-Sulfuric Acid Mixture.—Place 500 cc. of ethyl alcohol in a flask and slowly add 500 cc. of concentrated H_2SO_4. On account of the heat of the reaction, the flask should be well shaken and cooled in a stream of cold water during the addition of the acid. Use glass-stoppered bottle.

Aluminium Sulfate, 0.3M.—Dissolve 200 grams of $Al_2(SO_4)_3.18H_2O$ in 1 liter of warm water.

Ammonium Acetate, 10 Per Cent.—Dissolve 100 grams of $NH_4C_2H_3O_2$ in 900 cc. of water.

Ammonium Acetate, 50 Per Cent.—Dissolve 500 grams of $NH_4C_2H_3O_2$ in 500 cc. of water. Mark bottle: "For use in (57*b*) only."

Ammonium Hydroxide, 15M.—Use the concentrated solution (28 per cent NH_3). Use glass-stoppered bottle.

Ammonium Iodide, M.—Dissolve 145 grams of NH_4I in 1 liter of water. The solution will turn brown, owing to oxidation by the air, but that does not matter.

[1] With the exceptions noted below, these reagents may be very conveniently kept in liter bottles fitted with one-holed stoppers carrying short glass tubes, as described under "Compounding Unknowns," page 120.

Ammonium Molybdate.—Dissolve 50 grams of molybdic anhydride, MoO_3, in a mixture of 125 cc. of water and 75 cc. of concentrated NH_4OH (sp. gr. = 0.90). Slowly add this mixture with constant stirring to a mixture of 250 cc. of concentrated HNO_3 and 550 cc. of water. Allow to stand in a warm place for several days, and then decant the clear solution. This solution is 0.35M in H_2MoO_4, 1M in NH_4NO_3, and 3M in HNO_3.

Ammonium Nitrate, M.—Dissolve 80 grams of NH_4NO_3 in 1 liter of water.

Ammonium Sulfate, M.—Dissolve 130 grams of $(NH_4)_2SO_4$ in 1 liter of water.

Ammonium Thiocyanate, M.—Dissolve 75 grams of NH_4SCN in 1 liter of water.

Amyl Alcohol-Ether Mixture.—Add 350 cc. of amyl alcohol to 650 cc. of ethyl ether. Keep in glass-stoppered bottle. Mark "For use in Co Test Only."

Antimony Trichloride, 0.4M.—Dissolve 56.5 grams of $SbCl_3$ in 70 cc. of concentrated HCl and dilute to 1 liter. Add a little HCl to dissolve any turbidity.

Arsenic Trichloride, 0.2M.—Dissolve 20 grams of As_2O_3 in 120 cc. of hot concentrated HCl, and dilute to 1 liter.

Barium Nitrate, 0.4M.—Dissolve 95 grams of $Ba(NO_3)_2$ in 1 liter of warm water.

Bismuth Nitrate, 0.1M.—Dissolve 48 grams of $Bi(NO_3)_3$ in 50 cc. of concentrated HNO_3 and dilute to 1 liter. If a turbidity appears, add more HNO_3.

Cadmium Nitrate, 0.5M.—Dissolve 154 grams of $Cd(NO_3)_2.4H_2O$ in 1 liter of water.

Calcium Chloride, 0.5M.—Dissolve 110 grams of $CaCl_2.6H_2O$ in 1 liter of water.

Calcium Hydroxide (saturated solution).—Slake 3 or 4 grams of high-grade quicklime with excess of warm water. Add 1 liter of water, shake thoroughly, and filter.

Calcium Nitrate, M.—Dissolve 236 grams of $Ca(NO_3)_2.4H_2O$ in 1 liter of water.

Calcium Sulfate (saturated solution).—To 1 liter of water add 6 cc. of dilute H_2SO_4 and 2 grams of precipitated $CaCO_3$. Shake thoroughly and allow to stand for an hour. If there is no undissolved residue, or if the solution is still acid to litmus, add more $CaCO_3$ and shake again. Filter.

Carbon Disulfide.—Keep in glass-stoppered bottle.

Chlorine Solution (saturated).—Bubble a current of chlorine gas through a liter of water until the latter is saturated. (Hood). The gas is most conveniently obtained from a cylinder of compressed chlorine. If this is not available, the gas may be prepared by placing some solid $KMnO_4$ in a small generator fitted with a dropping funnel and a delivery tube, and allowing concentrated HCl from the funnel to drip slowly upon the $KMnO_4$. Keep the solution in a brown, glass-stoppered bottle.

Chromium Chloride, 0.2M.—Dissolve 53 grams of $CrCl_3.6H_2O$ in 20 cc. of concentrated HCl and 980 cc. of water.

Cobalt Nitrate, 0.2M.—Dissolve 58 grams of $Co(NO_3)_2.6H_2O$ in 1 liter of water.

Copper Nitrate, 0.2M.—Dissolve 59 grams of $Cu(NO_3)_2.6H_2O$ in 1 liter of water.

Copper Sulfate, M.—Dissolve 250 cc. of $CuSO_4.5H_2O$ in 1 liter of water.

Ether.—Use ethyl ("sulfuric") ether. Keep in glass-stoppered bottle.

Ferric Chloride, 0.4M.—Dissolve 108 grams of $FeCl_3.6H_2O$ in 10 cc. of concentrated HCl and 990 cc. of water.

Ferric Sulfate, 0.2M.—Dissolve 112 grams of $Fe_2(SO_4)_3.9H_2O$ in 20 cc. of dilute H_2SO_4 and 980 cc. of water.

Ferrous Sulfate, M.—Dissolve 392 grams of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in 500 cc. of dilute H_2SO_4 and 500 cc. of water.

Hydrogen Peroxide.—Use ordinary commercial solution (3 per cent). Keep in glass-stoppered bottle.

Lead Chloride (saturated solution).—Dissolve 11 grams of $PbCl_2$ in 1 liter of hot water. Decant from any precipitate.

Lead Nitrate, 0.5M.—Dissolve 165 grams of $Pb(NO_3)_2$ in 1 liter of water.

Magnesia Mixture.—Dissolve 130 grams of $Mg(NO_3)_2.6H_2O$ and 240 grams of NH_4NO_3 in 500 cc. of water, add 35 cc. of 6M NH_4OH, and dilute to 1 liter. This solution is 0.5M in $Mg(NO_3)_2$ and 3M in NH_4NO_3.

Magnesium Nitrate, 0.5M.—Dissolve 130 grams of $Mg(NO_3)_2.6H_2O$ in 1 liter of water.

Manganous Nitrate, 0.5M.—Dissolve 144 grams of $Mn(NO_3)_2.6H_2O$ in 1 liter of water.

Mercuric Chloride, 0.2M.—Dissolve 54 grams of $HgCl_2$ in 1 liter of water.

Mercuric Nitrate, 0.2M.—Dissolve 68 grams of $Hg(NO_3)_2.H_2O$ in 1 liter of water.

Mercurous Nitrate, 0.5M.—Dissolve 280 grams of $Hg_2(NO_3)_2.2H_2O$ in 300 cc. of concentrated HNO_3 and 700 cc. of water.

Nickel Chloride, 0.5M.—Dissolve 118 grams of $NiCl_2.6H_2O$ in 1 liter of water.

Nickel Nitrate, 0.3M.—Dissolve 83 grams of $Ni(NO_3)_2.6H_2O$ in 1 liter of water.

Oxalic Acid (saturated solution).—Dissolve 160 grams of $H_2C_2O_4.2H_2O$ in 1 liter of hot water. Cool, decant.

Potassium Arsenate, 0.2M.—Dissolve 51 grams of K_3AsO_4 in 1 liter of water.

Potassium Bromide, M.—Dissolve 120 grams of KBr in 1 liter of water.

Potassium Chloride, M.—Dissolve 75 grams of KCl in 1 liter of water.

Potassium Chromate, 0.5M.—Dissolve 97 grams of K_2CrO_4 in 1 liter of water.

Potassium Ferricyanide, 0.3M.—Dissolve 100 grams of $K_3Fe(CN)_6$ in 1 liter of water.

Potassium Hydrogen Tartrate (saturated solution).—Add 1 liter of warm water to 7 grams of $KHC_4H_4O_6$, shake thoroughly, and filter.

Potassium Iodide, M.—Dissolve 166 grams of KI in 1 liter of water.

Potassium Permanganate, 0.1M.—Dissolve 16 grams of $KMnO_4$ in 1 liter of water.

Potassium Sodium Tartrate (Rochelle salt), 0.25M.—Dissolve 70 grams of $KNaC_4H_4O_6.4H_2O$ in 1 liter of water.

Potassium Sulfate, 0.5M.—Dissolve 87 grams of K_2SO_4 in 1 liter of warm water.

Sodium Acetate, 3M.—Dissolve 408 grams of $NaC_2H_3O_2$ in 1 liter of hot water.

Sodium Arsenite, M.—Add 100 grams of As_2O_3 to 500 cc. of 6M NaOH, boil gently for 10 or 15 minutes, and dilute to 1 liter. After standing, decant the clear solution from any residue.

Sodium Carbonate, M.—Dissolve 106 grams of anhydrous Na_2CO_3 in 1 liter of water.

Sodium Chloride, M.—Dissolve 58.5 grams of NaCl in 1 liter of water.

Sodium Hypochlorite, 0.5M.—Dilute 135 cc. of 6M NaOH to 1 liter and pass chlorine into the mixture until it is almost neutral to red litmus paper. Keep in a brown glass bottle. A solution of bleaching powder may be used instead of NaOCl, and is much easier to prepare.

Sodium Hydroxide, 6M.—Dissolve 250 grams of NaOH "purified by alcohol" in 1 liter of water.

Sodium Nitrate, M.—Dissolve 85 grams of $NaNO_3$ in 1 liter of water.

Sodium Nitrite, M.—Dissolve 69 grams of $NaNO_2$ in 1 liter of water.

Sodium Silicate.—Dilute 50 cc. of water glass to 1 liter. If a sediment forms on standing, decant the clear liquid.

Sodium Sulfide, M.—Dissolve 240 grams of $Na_2S.9H_2O$ in 1 liter of water.

Sodium Tetraborate (Borax), 0.1M.—Dissolve 40 grams of $Na_2B_4O_7.10H_2O$ in 1 liter of water.

Sodium Thiosulfate, 0.5M.—Dissolve 125 grams of $Na_2S_2O_3.5H_2O$ in 1 liter of water.

Stannic Chloride, 0.2M.—Dissolve 52 grams of $SnCl_4$ in 100 cc. of concentrated HCl and dilute to 1 liter.

Stannous Chloride, 0.5M.—Dissolve 115 grams of $SnCl_2.2H_2O$ in 170 cc. of concentrated HCl, and dilute to 1 liter. A little granulated tin kept in the bottle will prevent oxidation to $SnCl_4$.

Strontium Nitrate, 0.5M.—Dissolve 142 grams of $Sr(NO_3)_2.4H_2O$ in 1 liter of water.

Strontium Sulfate (saturated solution).—To 1 liter of water add 6 cc. of dilute H_2SO_4 and 2 grams of precipitated $SrCO_3$. Shake thoroughly and allow to stand for an hour. If there is no undissolved residue, or if the solution is still acid to litmus, add more $SrCO_3$ and shake again. Filter.

Zinc Nitrate, 0.3M.—Dissolve 89 grams of $Zn(NO_3)_2.6H_2O$ in 1 liter of water.

Solids

Aluminium (wire cut into pieces weighing approximately 0.05 gram).
Ammonium chloride.
Asbestos (high-grade asbestos fiber, shredded and suspended in water).
Borax.
Broken tile (small pieces)
Calcium fluoride (powdered).
Calcium phosphate (powdered).
Dolomite (powdered).
Glass wool.
Iron filings.
Iron pyrites (powdered).
Lead dioxide.
Manganese dioxide, c. p.

Microcosmic salt ($NaNH_4HPO_4$).
Potassium bromide.
Potassium chlorate, c. p.
Potassium dichromate.
Potassium hydrogen sulfate.
Silica (powdered).
Sodium acetate (crystals).
Sodium carbonate (anhydrous, c. p.).
Sodium chloride.
Sodium fluoride.
Sodium nitrate.
Sodium nitrite (crystals).
Sodium oxalate.
Sodium-potassium carbonate.
Sodium sulfide (keep in rubber-stoppered bottle).
Sodium sulfite.
Tartaric acid (powdered).
Tin (granulated).
Zinc dust.

Storeroom

Alcohol (Ethyl), 95 per cent.

Alizarine.—Dissolve 0.01 gram in 100 cc. of 95 per cent C_2H_5OH, and keep in a bottle provided with a medicine dropper.

Dimethylglyoxime, 0.1M.—Dissolve 12 grams of the solid in 1 liter of 95 per cent C_2H_5OH.

Fluosilicic Acid..—Reagent H_2SiF_6 (7.5 per cent)

Perchloric Acid.—Use the 60 per cent solution. The so-called "dropping bottles," fitted with grooved glass stoppers, are very convenient for dispensing this reagent.

Potassium Iodide (crystals).

Sodium Cyanide, M.—Dissolve 50 grams of NaCN in 1 liter of water.

Sodium Peroxide.—Issue on watch glasses brought by the student.

Starch Paper.—Dip strips of filter paper in boiling starch solution. Dry, and keep in stoppered bottle.

Turmeric Paper (small strips).

HYDROGEN SULFIDE GENERATORS

One of the most troublesome problems in Qualitative Analysis is providing a constant supply of H_2S gas. Certain comments are deemed timely.

The use of small individual generators is discouraged, as not only inefficient, but dangerous. These generators are usually of the "continuous" type, and run until the acid is consumed, regardless of whether the gas is being absorbed or not. The storage of such a generator in a student locker may fill the locker with a very dangerous concentration of the gas.

Kipp generators may be moderately satisfactory for small sections, provided that they are equipped with a number of cocks, so that several students may use the gas at the same time. They are altogether inadequate, however, when large groups of students are to be supplied.

The two following plans have been used at the University of Illinois, and have been found to be very satisfactory for gas production on a large scale:

A is a cylindrical tank of glazed stoneware, about 30 cm. in diameter and 90 cm. high, which serves as a reservoir for commercial HCl. It is placed upon a platform so that the acid will run freely into the tanks *BB*. The

acid may be easily transferred from a carboy to this tank by fitting the neck of the former with a rubber stopper carrying two tubes—a short one, which may be connected with the compressed air system, and a longer one reaching to the bottom of the carboy, which is connected with rubber tubing leading to the acid tank. By applying air pressure, the acid is easily forced into the tank. *BB* are two tanks of glazed stoneware, slightly larger than the acid tank, sitting on a lead-lined drain board connected with the acid sewer. These tanks have each three openings, as shown in the figure: *HH* near the bottom through which the acid is introduced; *EE* fitted with cocks, through which the spent acid is withdrawn; and *JJ* connected through the wash bottles *CC* to the gasometer *G* and the service main. A layer of coke or other inert material is placed in the bottom of the cells to a level just above the openings *EE*, and then lump FeS is introduced until they are

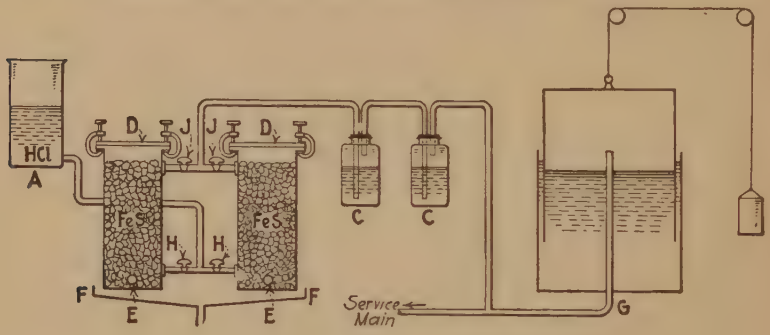

FIG. 12.—H_2S plant for large laboratories.

nearly full. The cells are covered with wooden lids, to the lower side of which is glued a heavy piece of "transite." A rubber gasket is placed between the lid and the cell, and the two are clamped together by clamps as shown in the figure, after which the joint is thoroughly luted with melted paraffin or universal wax. Only one of these tanks is used at a time; the second is provided for emergency service. *CC* are two large wash bottles of about 12 to 15 liters capacity for removing the $FeCl_2$ which is always present in the spray carried over by the H_2S. *G* is a storage tank of the gasometer type, and consists of a unit of glazed sewer tile about 90 cm. in diameter and 90 cm. high, into which an iron drum of slightly smaller size is placed in the usual way. The tile sits on a cement base, and the interior has been thoroughly waterproofed with tar so as to make it resistant to chemical attack. By means of counterpoises not shown in the figure, the weight of this drum is adjusted so as to maintain a gas pressure of about 20 to 25 cm. This drum should be carefully painted with high-grade acidproof paint at least once a year. Before applying the paint, the drum should be scraped clean and all iron rust removed. Every morning the spent acid is drained, and enough fresh acid is run into the FeS tank to fill the gasometer with H_2S. In case the amount of gas required is very large, a second gasom-

eter may be provided. This apparatus requires a minimum of attention, and a charge of FeS is sufficient for a run of six months or more.

A system for generating H_2S on a somewhat smaller scale is shown in Fig. 13. *A* is a large aspirator bottle, with a capacity of about 15 liters, which serves as a reservoir for the commercial HCl. It is placed on a shelf or platform about 100 cm. above the sink on which the generator bottle *B* stands. The trap in the tube between *A* and *B* prevents the escape of H_2S into the room. *B* is a wide-mouthed aspirator bottle, containing at the

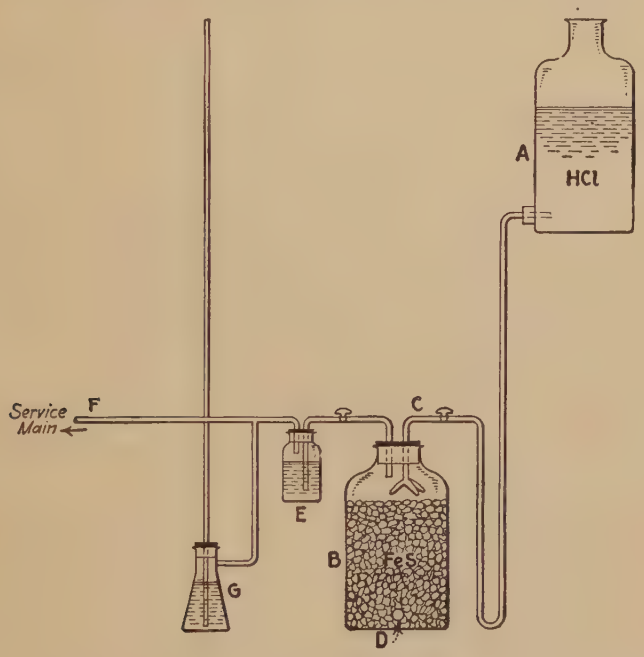

FIG. 13.—H_2S plant for medium-sized laboratories.

bottom a layer of coke or other inert granular material thick enough to cover the opening *D*. Lump FeS is introduced until the bottle is about three-fourths full. The tube *C* is provided with a stop cock, and its lower end is in the form of a triple jet, through which fresh acid drips whenever the gas pressure becomes low. *D* is a stoppered vent through which the waste $FeCl_2$ solution is withdrawn. From *B* the gas passes through the wash bottle *E* to the service line *F*. *G* is a large filter flask fitted with a glass tube about 100 cm. long, and serves to regulate the gas pressure in the leads.

Large generator systems for H_2S, such as those described above, should be kept in locked rooms or cupboards, where their adjustment cannot be tampered with by good-intentioned, but incapable, students.

Either iron or lead pipes may be used for distributing the gas over the laboratory. The latter material may cost more, but will probably pay for itself in longer service. Figure 14 shows the arrangement of H_2S openings for one of the gas lines in a hood. *AA* is the gas main, consisting of a 1-in. lead pipe, tapped at interval of about 30 cm. with short pieces of ⅛-in. lead pipe. These are connected to glass stop cocks by short rubber tubes, which

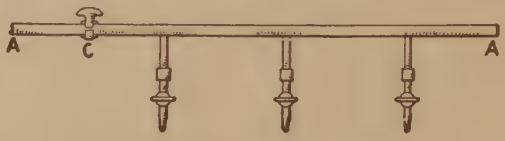

FIG. 14.—Service cocks in a H_2S line.

are tightly wired on by a double turn of copper wire. The arms of the glass cock should be short, so as to make the whole apparatus as stable and unbreakable as possible. The lower arms of the glass cocks should be slightly drawn out, so as to make it easy to slip on the rubber tubing of the precipitation flasks. The whole arrangement is made more stable by fixing the leads and cocks on a board, conveniently inclined, and strapping each cock in place by means of a lead strap. By all means place an emergency cock *C* in the main lead, so that in case of breakage or leakage the gas may be promptly shut off. Preferably, this emergency cut-off should be outside of the hood.

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